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THE HALF-PERIODS OF ACTINIUM B, ACTINIUM C", AND URANIUM X_1[1]

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Abstract

From measurements of the β-ray intensities by ionization at different times and semilogarithmic plots of these intensities against the time, the half-periods of actinium B, actinium C", and uranium X_1 were found to be 36.1 ± 0.2 min., 4.76 ± 0.02 min., and 24.1 ± 0.2 days, respectively.

In the course of some work (5) on the end-points of β-spectra, the half-periods of actinium B, actinium C", and uranium X_1 were determined with sufficient accuracy to be worth recording. The experimental details are given in the previous paper (5). The β-ray activity of a source was measured at different times by means of the ionization produced in a cylindrical steel chamber, 15.5 cm. long and of 13 cm. inside diameter. The gas in the chamber was carbon dioxide at a pressure of one atmosphere. A potential difference of 270 volts was maintained between the steel wall and a small axial wire, which was connected to a Compton electrometer. The ionization current is directly proportional to the observed rate of deflection of the electrometer needle when allowance is made for the effect of the initial oscillatory nature of the rate of deflection as a function of the time (5).

The logarithms of the β-ray activities were plotted against the times from the beginning of measurements to the mid-points of the readings. No error is introduced if the duration of the observation is short in comparison with the half-period. This condition was fulfilled in nearly every case. The exceptions were a few of the readings taken with sources of actinium C". Corrections were calculated from the exponential law of decay and applied to these readings so that they also could be plotted without error at their mid-points of time. In each case the half-period was obtained from the slope of the straight line of the graph.

Actinium B

The half-period of actinium B has been determined by at least ten experimenters with concordant results. The extreme values of the last seven

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determinations are 35.7 and 36.4 min. and of the last four, 36.0 and 36.2 min., as seen in a list compiled by Meyer and Schweidler (4, p. 482). While the average, 36.1 min., needs no further confirmation, the writer's values are presented here to show that systematic errors were eliminated in this case and therefore likely eliminated also in the cases of actinium C'' and uranium X_1.

Actinium $(B + C)$ was collected by recoil when aluminium discs were exposed to actinon for several hours. The sources were covered with mica to prevent loss of active deposit by α-ray recoil during the measurements. From the theory of successive transformations, the β-activity decays exponentially with the half-period of actinium B after 40 min. Measurements with each source were continued for three or four hours. In eight trials the extreme values of the half-period were 35.8 and 36.4 min., and the average value was 36.1 ± 0.2 min. The error attached is the average of the residuals obtained by subtracting the individual values from the average half-period. When the period of collection of the active deposit was limited to 10 or 15 hr., no corrections were found to be necessary for impurities of long half-period.

Actinium C''

There are only three published determinations of the half-period of actinium C'', and these are not in particularly good agreement. When Hahn and Meitner (2) discovered actinium C'' they made six measurements of its half-period. The extreme values were 5.05 and 5.4 min., and the average was 5.1 ± 0.1 min. Using 150 sources, Kovářik (3) found the half-period to lie between 4.60 and 4.85 min. and to have the average value 4.71 min. Finally, Albrecht (1) studied the decay of nine sources for about 20 min. each and obtained 4.76 ± 0.02 min.

In the present work the sources were prepared by recoil in air on to aluminium discs from the active deposit on polished nickel discs. The β-activity of each source was measured for 20 to 30 min. The half-periods obtained from the decay graphs of the first 10 trials lay between 4.63 and 4.83 min. and had an average of 4.76 ± 0.05 min. Seven more sources were used, under the best of conditions, and the half-periods were found to lie between 4.74 and 4.77 min. and to have an average of 4.76 ± 0.01 min. As a result of all the measurements, 4.76 ± 0.02 min. is adopted. No trace of any radioactive substance of long half-period was found.

Uranium X_1

The later published values of the half-period of uranium X_1 are 23.8 and 24.5 days (4, p. 377; 6), with greater emphasis on the latter.

In the present work the uranium X was so strong at first that its β-activity could be measured only after reduction by sheets of aluminium. It was an easy matter later to study the absorption of the β-rays in aluminium and to estimate the earlier intensities of the source without absorbers. Table I shows the β-ray intensities at various times.

TABLE I

β-RAY INTENSITIES

Time, days	0	97	118	141	152	174	233
β-intensity, cm./min.	13,330	769	432	220	166	87.7	15.8

Two types of corrections have been applied. In order to avoid errors due to changes in the sensitivity of the electrometer, a preparation of radium (D + E) in equilibrium was used as a standard source, and the uranium X was compared with it on each occasion. Small corrections for the decay of the radium D were applied.

The second type of corrections was necessary on account of a radioactive impurity in the preparation of uranium X. By a comparison of the penetrating power of the β-rays from the preparation when it was freshly prepared with that after 174 and 233 days, it was found that the penetrating power decreased with age. Actinium seemed to be a probable impurity on account of its well known generic relation to uranium. Moreover, the penetrating power of the β-rays from the preparation of uranium X after 233 days could be quantitatively accounted for on the assumption that 19.5% of the β-activity was due to actinium and its products, and 80.5% to uranium X. This calculation was possible since the absorption in aluminium of the β-rays of actinium and its products had been studied previously. The later β-ray activities of the preparation of uranium X have therefore been reduced by a constant amount to allow for the β-rays of actinium and its products.

From the semilogarithmic plot of the data in Table I the half-period of uranium X_1 is 24.1 $\pm$ 0.2 days.

Acknowledgments

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THE EQUILIBRIUM OF A THIN COMPRESSIBLE MEMBRANE[1]

By G. E. Hay[2]

Abstract

An investigation has been made of the equilibrium of a thin incompressible elastic membrane lying between two rigid bodies, one fixed and the other mobile. The present paper concerns the corresponding problem for a compressible membrane.

Membranes are divided mathematically into four classes according as their compressibility is (i) finite, (ii) small, (iii) very small, (iv) so small that the membrane may be considered as incompressible. The movable boundary is assigned a rigid body displacement. By the introduction of approximation based on the thinness of the membrane a determination of the resulting stress, strain and displacement is made for each of the above four classes of membranes.

1. Introduction

In some previous papers J. L. Synge (6, 7, 8) considered the elastic equilibrium of thin curved membranes of incompressible material, with application to the periodontal membrane or pericementum which fills the space between the tooth and the jaw-bone and is attached to both. It was later pointed out by J. N. Goodier that a compressibility even as small as that of water introduced terms comparable with those retained in the theory as developed on the assumption of incompressibility. The elastic equilibrium of thin flat compressible membranes was then considered by J. L. Synge (9). The present work deals with the equilibrium of thin curved compressible membranes, and in a later paper (5) the theory will be applied to a compressible periodontal membrane. In view of this application the theory will be developed for membranes bounded by two rigid bodies, of which one is fixed and the other is movable. The edge of the membrane is subject to atmospheric pressure. A determination will be made of the stress in the membrane and the displacement of the movable boundary when that boundary is subjected to assigned force systems.

2. Notation and Equations of Equilibrium of a Homogeneous Isotropic Elastic Medium

The points of the elastic medium will be referred to the curvilinear co-ordinate system x^i $(i=0,1,2)$. Latin indices will stand for the range 0,1,2, Greek indices for the range 1,2, and in accordance with the usual convention summation over either of these ranges will be signified by factors with repeated indices except where such indices are enclosed in brackets.

The line-element will be of the form

$$(2.1) \qquad\qquad ds^2 = a_{ij}dx^i dx^j,$$

and A_i will denote the operation of taking the covariant derivative with respect to a_{ij}. The contravariant derivative will then be

$$(2.2) \qquad A^i = a^{ij} A_j ,$$

where a^{ij} is the cofactor of a_{ij} in the determinant $| a_{ij} |$ divided by that determinant. Partial differentiation will be indicated in the two ways

$$(2.3) \qquad \frac{\partial U}{\partial x^i} = U_{,i} ,$$

where U is any function containing x^i. Thus for an invariant V,

$$(2.4) \qquad A_i V = V_{,i} , \quad A^i V = a^{ij} V_{,j} ,$$

and for the vector V^j or $V_i (= a_{jk} V^k)$,

$$(2.5) \qquad A_i V^j = V^j_{,i} + F^j_{ik} V^k_{,} \quad A_i V_j = V_{j,i} - F^k_{ij} V_k ,$$

where F^i_{jk} is the Christoffel symbol of the second kind,

$$(2.6) \qquad F^i_{jk} = \tfrac{1}{2} a^{il} (a_{lj,k} + a_{kl,j} - a_{jk,l}) .$$

For a mixed tensor $V_k^{\cdot j}$,

$$(2.7) \qquad A_i V_k^{\cdot j} = V_{k,i}^{\cdot j} + F^j_{il} V_k^{\cdot l} - F^l_{ik} V_l^{\cdot j} .$$

The (infinitesimal) components of displacement will be denoted by u^i, and hence the covariant components of strain are*

$$(2.8) \qquad e_{ij} = \tfrac{1}{2} (A_i u_j + A_j u_i) .$$

Since the medium is homogeneous and isotropic the stress-strain relations are

$$(2.9) \qquad T_{ij} = \frac{E}{1+\sigma} \left(e_{ij} + \frac{\sigma}{1-2\sigma} \theta a_{ij} \right) ,$$

where T_{ij} are the components of stress, E is Young's modulus, σ is Poisson's ratio and

$$(2.10) \qquad \theta = e_i^{\cdot i} = A_i u^i :$$

θ is called the cubical dilatation. From (2.9),

$$(2.11) \qquad \Theta = \frac{E}{1-2\sigma} \theta, \qquad \Theta = T_i^{\cdot i} .$$

In the absence of body forces the equations of equilibrium are

$$(2.12) \qquad A_j T_i^{\cdot j} = 0 .$$

Since the space is Euclidean $(A_i A_j = A_j A_i)$, substitution in (2.12) from (2.8), (2.9) and (2.10) leads to the following result:—

I. The equations of equilibrium of an elastically homogeneous and isotropic medium acted on by no body forces are

$$(2.13) \qquad A^i \theta + (1-2\sigma) A^j A_j u^i = 0 , \qquad\qquad (i=0,1,2),$$

* A more detailed application of tensor notation to elasticity is given in Reference (1, p. 91).

where A^i and A_i denote the contravariant and covariant derivatives respectively, u^i are the components of displacement, θ is the cubical dilatation and σ is Poisson's ratio.

3. The Parameter of Approximation

To solve (2.13) approximation is introduced based on (*a*) the thinness of the membrane, (*b*) the smallness of the compressibility, in the way followed by Synge in (6) and (9) respectively.   The method of introducing thinness was also used by Birkhoff (2), Garabedian (3), and Goodier (4).
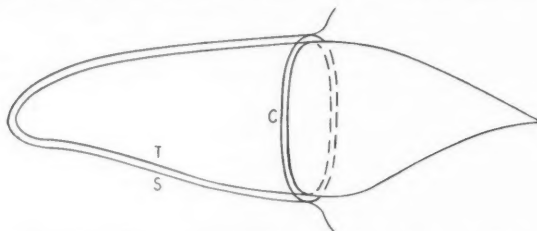

FIG. 1.   *Elastic system formed by a thin membrane attached to two rigid bodies S and T.*

Fig. 1 shows the elastic system under consideration.   It consists of a thin membrane bounded by and attached to two rigid bodies S and T, and having a free edge C.   The membrane is thin and a dimensionless parameter ϵ is introduced, defined by

$$(3.1) \qquad \epsilon = \frac{\text{average thickness of the membrane}}{\text{average length of the membrane}}$$

whence $\epsilon < < 1$.   When a length is comparable with $\epsilon^r \times$ *average length of the membrane*, $(r = 1, 2, \ . \ . \ )$, it will be said to be of order ϵ^r and when $r = 0$ it will be referred to as a "finite length".   Thus the thickness of the membrane is of order ϵ.

Since σ is Poisson's ratio, $1 - 2\sigma$ is dimensionless, vanishes for an incompressible medium and is a measure of the compressibility: it never exceeds unity and is frequently much smaller than unity: in any case it is permissible to write

$$(3.2) \qquad\qquad 1 - 2\sigma = k\epsilon^n, \qquad (n = 0, 1, 2, \ . \ . \ ) ,$$

where n is to be so chosen that k is comparable with unity.   The cases $n = 0, 1, 2$, and $n > 2$ will be considered successively: they refer respectively to finite compressibility, small compressibility, very small compressibility, and essential incompressibility, the reason for this last nomenclature being explained in §9.

4. The Normal Co-ordinate System.   Transformation of the Equations of Equilibrium

Fig. 2 shows a section of the membrane: S and T are the bounding rigid bodies.   The letters S and T can without ambiguity be used to denote their

surfaces: S is regarded as fixed and on it are chosen curvilinear co-ordinates x^α ($\alpha=1,2$). From a general point in the membrane, QN is drawn normal to S. Then by definition $x^0=QN$, whence x^i ($i=0,1,2$) define a set of curvilinear co-ordinates which are regular (*i.e.*, there is but one set of co-ordinates
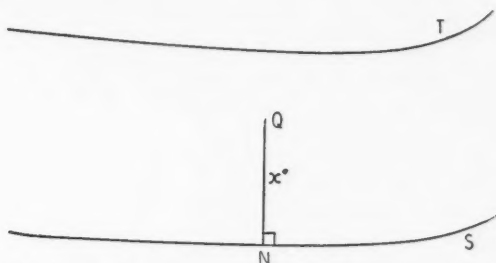

FIG. 2. *Section of the membrane and the bounding rigid bodies.*

for each point in the membrane) if QN is less than the smaller of the two principal radii of curvature of S at N. In view of the thinness of the membrane this inequality may be assumed to be satisfied.

The equation of T is

$$(4.1) \qquad x^0=h(x^1,x^2) ,$$

where $h(x^1,x^2)$ is a regular function over S: it is the thickness of the membrane. Then $0 \leqslant x^0 \leqslant h$ and the range of x^0 is small in comparison with the ranges of x^α ($\alpha=1,2$). Consequently ξ and τ are introduced, defined by

$$(4.2) \qquad x^0=\epsilon\xi , \qquad h(x^1,x^2)=\epsilon\tau(x^1,x^2) ,$$

where ϵ is the small parameter defined in (3.1). Then $0 \leqslant \xi \leqslant \tau$ and the ranges of ξ, x^1 and x^2 are all finite lengths.

From the nature of the co-ordinate system x^i ($i=0,1,2$),

$$(4.3) \qquad a_{\alpha 0}=0 , \qquad a_{00}=1 , \qquad a^{\alpha 0}=0 , \qquad a^{00}=1 .$$

Thus the Christoffel symbols are

$$(4.4) \qquad F^0_{00}=F^\alpha_{00}=F^0_{0\alpha}=0 , \qquad F^0_{\alpha\beta}=-\tfrac{1}{2}a_{\alpha\beta,0} , \qquad F^\alpha_{\beta 0}=\tfrac{1}{2}a^{\alpha\gamma}a_{\beta\gamma,0} .$$

It is noted that any Christoffel symbol with two or more zero indices vanishes. All the remaining Christoffel symbols are regular functions of x^0, x^1 and x^2; expansion in power series in x^0 gives

$$(4.5) \qquad F^i_{jk} = \sum_{m=0}^\infty \frac{1}{m!} \epsilon^m \xi^m F^i_{jk(m)} ,$$

where

$$(4.6) \qquad F^i_{jk(m)} = \left(\frac{\partial^m F^i_{jk}}{(\partial x^0)^m} \right)_{x^0=0} , \qquad 0!=1 \text{ (by definition)},$$

and $F^i_{jk(m)}$ are regular functions of x^1 and x^2.

Similarly

$$(4.7) \qquad a^{\alpha\beta} = \sum_{m=0}^{\infty} \frac{1}{m!} \, \epsilon^m \xi^m a^{\alpha\beta}_{(m)} \,, \quad a_{\alpha\beta} = \sum_{m=0}^{\infty} \frac{1}{m!} \, \epsilon^m \xi^m a_{\alpha\beta(m)} \,,$$

where

$$(4.8) \qquad a^{\alpha\beta}_{(m)} = \left(\frac{\partial^m a^{\alpha\beta}}{(\partial x^0)^m} \right)_{x^0=0} , \qquad a_{\alpha\beta(m)} = \left(\frac{\partial^m a_{\alpha\beta}}{(\partial x^0)^m} \right)_{x^0=0} .$$

Since

$$(4.9) \qquad \frac{\partial}{\partial x^0} = \frac{1}{\epsilon} \frac{\partial}{\partial \xi} \,,$$

then by (2.5)

$$(4.10) \quad \left\{ \begin{array}{ll} A_0 u^0 = \dfrac{1}{\epsilon} \dfrac{\partial u^0}{\partial \xi} \,, & A_0 u^\alpha = \dfrac{1}{\epsilon} \dfrac{\partial u^\alpha}{\partial \xi} + F^\alpha_{0\beta} u^\beta, \\[2ex] A_\alpha u^0 = u^0_{,\alpha} + F^0_{\alpha\beta} u^\beta, & A_\alpha u^\beta = u^\beta_{,\alpha} + F^\beta_{\alpha i} u^i, \end{array} \right.$$

and by (2.7),

$$(4.11) \quad \left\{ \begin{array}{l} A^0 A_0 u^0 = \dfrac{1}{\epsilon^2} \dfrac{\partial^2 u^0}{\partial \xi^2} \,, \\[2ex] A^0 A_0 u^\gamma = \dfrac{1}{\epsilon^2} \dfrac{\partial^2 u^\gamma}{\partial \xi^2} + \dfrac{2}{\epsilon} F^\gamma_{\beta 0} \dfrac{\partial u^\beta}{\partial \xi} + F^\gamma_{\beta 0,0} u^\beta + F^\gamma_{\beta 0} F^\beta_{\alpha 0} u^\alpha, \\[2ex] A^\alpha A_\alpha u^0 = a^{\alpha\beta} \left[-\dfrac{1}{\epsilon} F^0_{\alpha\beta} \dfrac{\partial u^0}{\partial \xi} + u^0_{,\alpha\beta} - F^\gamma_{\alpha\beta} u^0_{,\gamma} + F^0_{\beta\gamma} F^\gamma_{\alpha 0} u^0 \right. \\[2ex] \qquad\qquad \left. + 2 F^0_{\alpha\gamma} u^\gamma_{,\beta} + (F^0_{\alpha\delta,\beta} + F^0_{\beta\gamma} F^\gamma_{\alpha\delta} - F^\gamma_{\alpha\beta} F^0_{\gamma\delta}) u^\delta \right], \\[2ex] A^\alpha A_\alpha u^\gamma = a^{\alpha\beta} \left[-\dfrac{1}{\epsilon} F^0_{\alpha\beta} \dfrac{\partial u^\gamma}{\partial \xi} + 2 F^\gamma_{\alpha 0} u^0_{,\beta} \right. \\[2ex] \qquad\qquad + (F^\gamma_{\alpha 0,\beta} + F^\gamma_{\beta\delta} F^\delta_{\alpha 0} - F^\delta_{\alpha\beta} F^\gamma_{\delta 0}) u^0 + u^\gamma_{,\alpha\beta} + 2 F^\gamma_{\alpha\delta} u^\delta_{,\beta} \\[2ex] \qquad\qquad \left. - F^\delta_{\alpha\beta} u^\gamma_{,\delta} + (F^\gamma_{\alpha\delta,\beta} + F^\gamma_{\beta i} F^i_{\alpha\delta} - F^i_{\alpha\beta} F^\gamma_{i\delta}) u^\delta \right]. \end{array} \right.$$

From (4.10) the cubical dilatation θ is given by

$$(4.12) \qquad \theta = \frac{1}{\epsilon} \frac{\partial u^0}{\partial \xi} + u^\alpha_{,\alpha} + F^\alpha_{\alpha i} u^i .$$

Substitution from (4.11) in (2.13) produces the following:—

II. Relative to the co-ordinate system ξ, x^1, x^2 the equations of equilibrium are

$$(4.13) \qquad \frac{1}{\epsilon}\frac{\partial \theta}{\partial \xi} + (1-2\sigma)\left\{\frac{1}{\epsilon^2}\frac{\partial^2 u^0}{\partial \xi^2} + a^{\alpha\beta}\left[-\frac{1}{\epsilon}F^0_{\alpha\beta}\frac{\partial u^0}{\partial \xi} + u^0_{,\alpha\beta} - F^\gamma_{\alpha\beta}u^0_{,\gamma}\right.\right.$$

$$\left.\left. + F^0_{\beta\gamma}F^\gamma_{\alpha 0}u^0 + 2F^0_{\alpha\gamma}u^\gamma_{,\beta} + (F^0_{\alpha\delta,\beta} + F^0_{\beta\gamma}F^\gamma_{\alpha\delta} - F^\gamma_{\alpha\beta}F^0_{\gamma\delta})u^\delta\right]\right\} = 0,$$

$$(4.14) \qquad a^{\gamma\alpha}\theta_{,\alpha} + (1-2\sigma)\left\{\frac{1}{\epsilon^2}\frac{\partial^2 u^\gamma}{\partial \xi^2} + \frac{2}{\epsilon}F^\gamma_{\beta 0}\frac{\partial u^\beta}{\partial \xi} + [F^\gamma_{\delta 0,0} + F^\gamma_{\beta 0}F^\beta_{\delta 0}]u^\delta\right.$$

$$+ a^{\alpha\beta}\left[-\frac{1}{\epsilon}F^0_{\alpha\beta}\frac{\partial u^\gamma}{\partial \xi} + 2F^\gamma_{\alpha 0}u^0_{,\beta}\right.$$

$$+ (F^\gamma_{\alpha 0,\beta} + F^\gamma_{\beta\delta}F^\delta_{\alpha 0} - F^\delta_{\alpha\beta}F^\gamma_{\delta 0})u^0$$

$$+ u^\gamma_{,\alpha\beta} + 2F^\gamma_{\alpha\delta}u^\delta_{,\beta} - F^\delta_{\alpha\beta}u^\gamma_{,\delta}$$

$$\left.\left. + (F^\gamma_{\alpha\delta,\beta} + F^\gamma_{\beta i}F^i_{\alpha\delta} - F^i_{\alpha\beta}F^\gamma_{i\delta})u^\delta\right]\right\} = 0.$$

In these formulae ϵ is the dimensionless parameter defined in (3.1), u^i are the components of displacement within the membrane, a_{ij} and a^{ij} are respectively the covariant and contravariant forms of the fundamental tensor, F^i_{jk} are the Christoffel symbols defined in (2.6), θ is expressed by (4.12), a subscript preceded by a comma signifies partial differentiation as illustrated in (2.3), Greek indices have the range 1,2, and Latin indices have the range 0,1,2.

5. The Formal Process of Integration of the Equations of Equilibrium

It is required to solve (4.13) and (4.14) for the principal parts of u^i where $0 \leqslant \xi \leqslant \tau(x^1, x^2)$ and the range of values of x^1 and x^2 corresponds to the part of the solid T covered by the membrane. The boundary conditions are that $u^i = 0$ for $\xi = 0$, that for $\xi = \tau$ the values of u^i shall be equal to the components of the rigid body displacement of the solid T, and that over the edge of the membrane the normal stress shall be a constant pressure P.

It is assumed for all small values of ϵ that (4.13) and (4.14) admit of solutions which are expressible in power series in ϵ with coefficients which are regular functions of ξ, x^1 and x^2. The thickness of the membrane is of order ϵ and since u^i must be of higher order,

$$(5.1) \qquad u^i = \sum_{m=2}^{\infty} \epsilon^m u^i_{(m)},$$

where $u^i_{(m)}$ are finite.

The boundary conditions are as follows:—

$$(5.2) \quad \begin{cases} \text{for } \xi=0, \quad u^i=0, \\ \text{for } \xi=\tau, \quad u^i=\beta^i=\sum_{m=2}^{\infty} \epsilon^m \beta^i_{(m)}, \\ \text{the stress normal to } f(x^1,\ x^2)=0 \text{ is independent of } \epsilon \text{ and is a} \\ \text{pressure } P, \end{cases}$$

where β^i are the components of the rigid body displacement of T, $\beta^i_{(m)}$ are functions of x^1 and x^2 only and are comparable with any finite length, and $f(x^1, x^2)=0$ is the edge of the membrane: P will be assumed to be of the form

$$(5.3) \qquad\qquad P = \sum_{m=0}^{\infty} \epsilon^m P_{(m)},$$

where $P_{(0)}$, $P_{(1)}$, . . . are constants independent of ϵ.

From (2.5), (2.8), (4.2) and (4.4) the strain components and the dilatation are

$$(5.4) \quad \begin{cases} e_{00} = \dfrac{1}{\epsilon}\dfrac{\partial u^0}{\partial \xi}, \\[2mm] e_{\alpha 0} = \tfrac{1}{2}\left\{ a_{\alpha\beta}\left(\dfrac{1}{\epsilon}\dfrac{\partial u^\beta}{\partial \xi} + F^\beta_{0\gamma}u^\gamma\right)+u^0_{,\alpha}+F^0_{\alpha\beta}u^\beta\right\}, \\[2mm] e_{\alpha\beta} = \tfrac{1}{2}\left\{ a_{\beta\gamma}(u^\gamma_{,\alpha}+F^\gamma_{\alpha i}u^i)+a_{\alpha\gamma}(u^\gamma_{,\beta}+F^\gamma_{\beta i}u^i)\right\}, \\[2mm] \theta = \dfrac{1}{\epsilon}\dfrac{\partial u^0}{\partial \xi} + u^\alpha_{,\alpha}+F^\alpha_{\alpha i}u^i. \end{cases}$$

Using (4.5), (4.7) and (5.1), these can be expressed explicitly in ϵ, whence

$$(5.5) \quad \begin{cases} e_{00} = \epsilon\dfrac{\partial u^0_{(2)}}{\partial \xi} + \epsilon^2\dfrac{\partial u^0_{(3)}}{\partial \xi} + 0(\epsilon^3), \\[2mm] e_{\alpha 0} = \tfrac{1}{2}\left\{\epsilon a_{\alpha\gamma(0)}\dfrac{\partial u^\gamma_{(2)}}{\partial \xi}+0(\epsilon^2)\right\}, \\[2mm] e_{\alpha\beta} = \tfrac{1}{2}\left\{\epsilon^2[a_{\beta\gamma(0)}(u^\gamma_{(2),\alpha}+F^\gamma_{\alpha i(0)}u^i_{(2)}) \right. \\[2mm] \qquad\qquad \left. +a_{\alpha\gamma(0)}(u^\gamma_{(2),\beta}+F^\gamma_{\beta i(0)}u^i_{(2)})]+0(\epsilon^3)\right\}, \end{cases}$$

$$(5.6) \qquad\qquad \theta = \epsilon\theta_{(1)}+\epsilon^2\theta_{(2)}+ \ \text{-}\ \text{-}\ \text{-},$$

where

$$(5.7) \qquad \theta_{(1)} = \dfrac{\partial u^0_{(2)}}{\partial \xi}, \quad \theta_{(r)} = \dfrac{\partial u^0_{(r+1)}}{\partial \xi}+u^\alpha_{(r),\alpha}+\sum_{s=0}^{r-2}\dfrac{1}{s!}\ \xi^s F^\alpha_{\alpha i(s)}u^i_{(r-s)},$$

$$(r=2,\ 3,\ \text{-}\ \text{-}\ \text{-}\ ).$$

The system of stresses compatible with the strain (5.5) must remain finite as $\epsilon \to 0$. Using (2.11) and (3.2), the sum of the principal stresses is given by

$$(5.8) \qquad \Theta = \frac{E}{k\epsilon^n}(\epsilon\theta_{(1)} + \epsilon^2\theta_{(2)} + \; \cdot \; \cdot \; \cdot \;).$$

If $n = 0$ or 1, Θ (and also the stress components T_{ij}) remain finite as $\epsilon \to 0$. If $n = 2$ it is necessary that $\theta_{(1)} = 0$ and by (5.7), $u^0_{(2)}$ is then a function of x^1 and x^2 only. Thus $\beta^0_{(2)} = 0$ and hence since T is a rigid body $\beta^i_{(2)} = 0$. This is summed up as follows:—

III. If $n = 0$ or 1 the condition of finite stress is satisfied when u^i is of order ϵ^2. If $n = 2$ it is necessary that

$$(5.9) \qquad u^0_{(2)} = 0, \qquad \theta_{(1)} = 0, \qquad \beta^i_{(2)} = 0.$$

If $n > 2$, (5.9) must be satisfied and also

$$(5.10) \qquad \theta_{(r)} = \frac{\partial u^0_{(r+1)}}{\partial \xi} + u^\alpha_{(r),\alpha} + \sum_{s=0}^{r-2} \frac{1}{s!} \, \xi^s F^\alpha_{\alpha i(s)} u^i_{(r-s)} = 0,$$
$$(r = 2, 3, \; \cdot \; \cdot \; \cdot \; n-1).$$

In the absence of restrictions as regards the value of n, substitution in the equations of equilibrium (4.13) and (4.14) for $1 - 2\sigma$, F^i_{jk}, $a^{\alpha\beta}$, $a_{\alpha\beta}$ and u^i from (3.2), (4.5), (4.7) and (5.1) gives three equations each of which is (i) explicit in ϵ, (ii) a power series in ϵ, (iii) true for all small values of ϵ. Hence the coefficients of all powers of ϵ must vanish identically, and by equating to zero the coefficient of the lowest power of ϵ occurring in each equation three partial differential equations for the principal parts of the displacement are obtained. This is summed up as follows:—

IV. The differential equations for the principal parts of the displacement u^i ($i = 0,1,2$) are obtained by equating to zero the coefficient of the lowest power of ϵ occurring in (4.13) and in (4.14) after substitution has been carried out for $1 - 2\sigma$, F^i_{jk}, $a^{\alpha\beta}$, $a_{\alpha\beta}$ and u^i from (3.2), (4.5), (4.7) and (5.1).

6. The Case $n = 0$ (Finite Compressibility)

Upon taking $n = 0$ in (3.2) and carrying out the substitutions indicated in IV, one finds that the lowest power of ϵ occurring both in (4.13) and in (4.14) is ϵ^0 and that the corresponding coefficients give rise to the equations

$$(6.1) \qquad (1+k)\frac{\partial^2 u^0_{(2)}}{\partial \xi^2} = 0,$$

$$(6.2) \qquad k\frac{\partial^2 u^\alpha_{(2)}}{\partial \xi^2} = 0.$$

The following boundary conditions are obtained from (5.2):—

$$(6.3) \qquad \text{for} \qquad \xi = 0, \qquad u^i_{(2)} = 0,$$
$$(6.4) \qquad \text{for} \qquad \xi = \tau, \qquad u^i_{(2)} = \beta^i_{(2)},$$

(6.5)   the stress normal to $f(x^1, x^2) = 0$ is a constant pressure P, where $f(x^1, x^2) = 0$ is the edge of the membrane. Since $k \neq -1$, the solution of (6.1) and (6.2) subject to (6.3) and (6.4) is

$$(6.6) \qquad\qquad u_{(2)}^i = \xi \beta_{(2)}^i / \tau .$$

The boundary condition (6.5) has yet to be satisfied.

Substitution from (6.6) in (5.5) gives for the strain components and dilatation

$$(6.7) \quad \left\{ \begin{array}{l} e_{00} = \epsilon \beta_{(2)}^0 / \tau + 0(\epsilon^2) , \\[1.5ex] e_{\alpha 0} = \tfrac{1}{2} \epsilon a_{\alpha \gamma(0)} \beta_{(2)}^\gamma / \tau + 0(\epsilon^2) , \\[1.5ex] e_{\alpha \gamma} = \tfrac{1}{2} \epsilon^2 \xi \{ a_{\gamma \delta(0)} (\beta_{(2)}^\delta / \tau) ,_\alpha + a_{\alpha \delta(0)} (\beta_{(2)}^\delta / \tau) ,_\gamma \\[1.5ex] \qquad\qquad + (a_{\gamma \delta(0)} F_{\alpha i(0)}^\delta + a_{\alpha \delta} F_{\gamma i(0)}^\delta) (\beta_{(2)}^i / \tau) \} + 0(\epsilon^3) , \\[1.5ex] \theta = \epsilon \beta_{(2)}^0 / \tau + 0(\epsilon^2). \end{array} \right.$$

Since $1 - 2\sigma = k$, by (2.9) the stress components are

$$(6.8) \quad \left\{ \begin{array}{l} T_{00} = \dfrac{E(1-\sigma)}{(1+\sigma)(1-2\sigma)} \dfrac{\beta_{(2)}^0}{\tau} \epsilon + 0(\epsilon^2) , \\[2.5ex] T_{\alpha 0} = \dfrac{E}{2(1+\sigma)} \dfrac{\beta_{(2)}^\gamma}{\tau} a_{\gamma \alpha(0)} \epsilon + 0(\epsilon^2) , \\[2.5ex] T_{\alpha \gamma} = \dfrac{E\sigma}{(1+\sigma)(1-2\sigma)} \dfrac{\beta_{(2)}^0}{\tau} a_{\alpha \gamma(0)} \epsilon + 0(\epsilon^2) . \end{array} \right.$$

If the outward normal to the edge of the membrane is denoted by the unit vector $(0, n^1, n^2)$, the covariant components of the stress across this edge are $T_i = T_{i\alpha} n^\alpha$, whence

$$(6.9) \quad \left\{ \begin{array}{l} T_0 = \dfrac{E}{2(1+\sigma)} \dfrac{\beta_{(2)}^\alpha}{\tau} n^\gamma a_{\alpha \gamma(0)} \epsilon + 0(\epsilon^2) , \\[2.5ex] T_\alpha = \dfrac{E\sigma}{(1+\sigma)(1-2\sigma)} \dfrac{\beta_{(2)}^0}{\tau} n^\gamma a_{\gamma \alpha(0)} \epsilon + 0(\epsilon^2) . \end{array} \right.$$

The pressure P over the edge of the membrane is expressed by (5.3) and if the stress system (6.9) is to be such a pressure it is necessary that

$$(6.10) \qquad a_{\alpha \gamma(0)} \beta_{(2)}^\alpha n^\gamma = 0, \quad \frac{E\sigma}{(1+\sigma)(1-2\sigma)} \frac{\beta_{(2)}^0}{\tau} = -P_{(1)} , \quad P_{(0)} = 0 .$$

It is possible to satisfy these conditions only when $P_{(0)} = P_{(1)} = \beta_{(2)}^i = 0$. The method then breaks down since it is impossible to satisfy all the boundary conditions. However the strain and stress components given in (6.7) and (6.8) are valid throughout all the membrane except a narrow strip around the edge: this is taken into account by saying that in the case $n = 0$ there is an edge effect.

These results are summed up as follows, expressed explicitly in the small quantities, the ϵ-method having now served its purpose:—

V. For a thin curved membrane of finite compressibility there is an edge effect in a narrow strip around the edge of the membrane. In the rest of the membrane the principal parts of the displacement are

$$(6.11) \qquad\qquad u^i = \beta^i x^0 / h \,,$$

the principal parts of the strain and dilatation are

$$(6.12) \quad
\begin{cases}
e_{00} = \beta^0 / h \,, \qquad e_{\alpha 0} = \tfrac{1}{2} a_{\alpha\gamma} \beta^\gamma / h \,, \\[2mm]
e_{\alpha\gamma} = \tfrac{1}{2} x^0 \{ a_{\gamma\delta} (\beta^\delta/h)_{,\alpha} + a_{\alpha\delta} (\beta^\delta/h)_{,\gamma} \\[2mm]
\qquad\qquad + (a_{\gamma\delta} F^\delta_{\alpha i} + a_{\alpha\delta} F^\delta_{\gamma i})(\beta^i/h) \} \,, \\[2mm]
\theta = \beta^0 / h \,,
\end{cases}$$

and the principal parts of the stress are

$$(6.13) \quad
\begin{cases}
T_{00} = \dfrac{E(1-\sigma)}{(1+\sigma)(1-2\sigma)} \dfrac{\beta^0}{h} \,, \qquad\qquad T_{\alpha 0} = \dfrac{E}{2(1+\sigma)} \dfrac{\beta^\gamma}{h} a_{\gamma\alpha} \,, \\[4mm]
T_{\alpha\gamma} = \dfrac{E\sigma}{(1+\sigma)(1-2\sigma)} \dfrac{\beta^0}{h} a_{\alpha\gamma} \,.
\end{cases}$$

In these formulae β^i are the components of the displacement of a point (x^1, x^2) on T and are of order ϵ^2, x^0 is the length of the normal to S, h is the thickness of the membrane, a_{ij} is the fundamental tensor, E is Young's modulus, σ is Poisson's ratio and ϵ is the small parameter defined in (3.1).

7. The Case $n=1$ (Small Compressibility)

Upon taking $n=1$ in (3.2) and carrying out the substitutions indicated in IV, it is found that the lowest power of ϵ occurring in (4.13) is ϵ^0 and in (4.14) is ϵ. The corresponding coefficients give rise to the equations

$$(7.1) \qquad\qquad \frac{\partial^2 u^0_{(2)}}{\partial \xi^2} = 0 \,,$$

$$(7.2) \qquad\qquad a^{\alpha\gamma}_{(0)} \frac{\partial}{\partial \xi} (u^0_{(2),\gamma}) + k \frac{\partial^2 u^\alpha_{(2)}}{\partial \xi^2} = 0 \,.$$

The following boundary conditions are obtained from (5.2):—

(7.3)   for $\xi = 0$, $u^i_{(2)} = 0$,

(7.4)   for $\xi = \tau$, $u^i_{(2)} = \beta^i_{(2)}$,

(7.5)   the stress normal to $f(x^1, x^2) = 0$ is a constant pressure P,

where $f(x^1, x^2) = 0$ is the edge of the membrane. Using (7.3) and (7.4), integration of (7.1) gives

$$(7.6) \qquad\qquad u_{(2)}^0 = \xi\beta_{(2)}^0/\tau ,$$

and upon substitution of this value of $u_{(2)}^0$ in (7.2) integration gives

$$(7.7) \qquad\qquad u_{(2)}^\alpha = \frac{\xi\beta_{(2)}^\alpha}{\tau} + \frac{(\tau-\xi)\xi}{2k}\, a_{(0)}^{\alpha\gamma}(\beta_{(2)}^0/\tau)_{,\gamma}$$

satisfying (7.3) and (7.4). The boundary condition (7.5) has yet to be satisfied.

Substitution from (7.6) and (7.7) in (5.5) gives for the strain components and dilatation

$$(7.8) \qquad \left\{ \begin{array}{ll} e_{00} = \epsilon\beta_{(2)}^0/\tau + 0(\epsilon^2) , & \\[2mm] e_{\alpha 0} = 0(\epsilon) , & e_{\alpha\gamma} = 0(\epsilon^2) , \\[2mm] \theta = \epsilon\beta_{(2)}^0/\tau + 0(\epsilon^2) . & \end{array} \right.$$

Since $1-2\sigma = k\epsilon$, so that $\sigma = \frac{1}{2}$ approximately, by (2.9) the stress components are

$$(7.9) \qquad \left\{ \begin{array}{l} T_{00} = E\beta_{(2)}^0/(3k\tau) + 0(\epsilon) , \\[2mm] T_{\alpha 0} = 0(\epsilon) , \\[2mm] T_{\alpha\gamma} = E\beta_{(2)}^0 a_{\alpha\gamma(0)}/(3k\tau) + 0(\epsilon) . \end{array} \right.$$

Thus the principal part of the stress is a finite pressure

$$(7.10) \qquad\qquad p = -E\beta_{(2)}^0/(3k\tau) ,$$

and to satisfy (7.5) it is necessary that

$$(7.11) \qquad\qquad P_{(0)} = -E\beta_{(2)}^0/(3k\tau) .$$

There is obviously an edge effect as in §6.

These results are summed up as follows:—

VI. For a thin curved membrane of small compressibility, $1-2\sigma$ being comparable with ϵ, there is an edge effect in a narrow strip around the edge of the membrane. In the rest of the membrane the principal parts of the displacement are

$$(7.12) \qquad \left\{ \begin{array}{l} u^0 = \dfrac{x^0\beta^0}{h} , \\[4mm] u^\alpha = \dfrac{x^0\beta^\alpha}{h} + \dfrac{(h-x^0)x^3}{2(1-2\sigma)}\, a^{\alpha\gamma}(\beta^c/h)_{,\gamma} , \end{array} \right.$$

and the principal part of the stress is a finite pressure

$$(7.13) \qquad p = -E\beta^0 / \{3h(1-2\sigma)\} .$$

In these formulae β^i are the components of the displacement of a point (x^1, x^2) on T and are of order ϵ^2, x^0 is the length of the normal to S, h is the thickness of the membrane, a_{ij} is the fundamental tensor, E is Young's modulus, σ is Poisson's ratio and ϵ is the small parameter defined in (3.1).

8. The Case $n=2$ (Very Small Compressibility)

This case is more interesting since, as it turns out, the membrane under consideration has the elastic properties of the periodontal membrane. The condition for finite stress (5.9) requires that

$$(8.1) \qquad u_{(2)}^0 = 0 , \qquad \theta_{(1)} = 0 , \qquad \beta_{(2)}^i = 0 .$$

Upon taking $n=2$ in (3.2) and carrying out the substitutions indicated in IV, it is found that the lowest power of ϵ occurring in (4.13) is ϵ and in (4.14) is ϵ^2. The corresponding coefficients give rise to the equations

$$(8.2) \qquad \frac{\partial \theta_{(2)}}{\partial \xi} = 0 ,$$

$$(8.3) \qquad a_{(0)}^{\alpha\gamma}\theta_{(2),\gamma} + k \frac{\partial^2 u_{(2)}^{\alpha}}{\partial \xi^2} = 0 ,$$

where from (5.7),

$$(8.4) \qquad \theta_{(2)} = \frac{\partial u_{(3)}^0}{\partial \xi} + u_{(2),\alpha}^{\alpha} + F_{\alpha\gamma(0)}^{\alpha} u_{(2)}^{\gamma} .$$

The following boundary conditions are obtained from (5.2):—

$$(8.5) \qquad \text{for} \qquad \xi = 0 , \qquad u_{(3)}^0 = u_{(2)}^{\alpha} = 0 ,$$

$$(8.6) \qquad \text{for} \qquad \xi = \tau , \qquad u_{(3)}^0 = \beta_{(3)}^0 , \qquad u_{(2)}^{\alpha} = 0 ,$$

(8.7) the stress normal to $f(x^1, x^2) = 0$ is a constant pressure P, where $f(x^1, x^2) = 0$ is the edge of the membrane.

From (8.2) it is seen that $\theta_{(2)}$ is a function of x^1 and x^2 only, and hence (8.3) has the solution

$$(8.8) \qquad k u_{(2)}^{\alpha} = \tfrac{1}{2}(\tau - \xi) \xi a_{(0)}^{\alpha\gamma}\theta_{(2),\gamma} ,$$

satisfying (8.5) and (8.6). This value for $u_{(2)}^{\alpha}$ is substituted in (8.4), and since the resulting equation is explicit in ξ easy integration gives

$$(8.9) \qquad k u_{(3)}^0 = -\frac{1}{12}\xi^2 (3\tau - 2\xi)\{(a_{(0)}^{\alpha\gamma}\theta_{(2),\gamma})_{,\alpha} + F_{\alpha\gamma(0)}^{\alpha} a_{(0)}^{\gamma\delta}\theta_{(2),\delta}\}$$
$$- \frac{1}{4}\xi^2 a_{(0)}^{\alpha\gamma}\theta_{(2),\gamma}\tau_{,\alpha} + k\xi\theta_{(2)} ,$$

satisfying (8.5).   To satisfy (8.6) it is necessary that

$$(8.10) \qquad k\beta^0_{(3)} = -\frac{\tau^3}{12} \left\{ (a^{\alpha\gamma}_{(0)}\theta_{(2),\gamma})_{,\alpha} + F^\alpha_{\alpha\gamma(0)} a^{\gamma\delta}_{(0)}\theta_{(2),\delta} \right\}$$
$$- \frac{1}{4}\tau^2 a^{\alpha\gamma}_{(0)}\theta_{(2),\gamma}\tau_{,\alpha} + k\tau\theta_{(2)} ,$$

and upon rearranging it is seen that $\theta_{(2)}$ satisfies the partial differential equation

$$(8.11) \qquad (\tau^3 a^{\alpha\gamma}_0 \theta_{(2),\gamma})_{,\alpha} + \tau^3 F^\alpha_{\alpha\gamma(0)} a^{\gamma\delta}_{(0)}\theta_{(2),\delta} = 12k(\tau\theta_{(2)} - \beta^0_{(3)}) .$$

When $\theta_{(2)}$ has been found to satisfy this equation, the principal parts of the displacement follow from (8.8) and (8.9).

Thus using (5.4), the components of strain may be calculated.   They are of the following orders:—

$$(8.12) \qquad e_{00} = 0(\epsilon^2), \qquad e_{\alpha 0} = 0(\epsilon), \qquad e_{\alpha\gamma} = 0(\epsilon^2).$$

The dilatation is

$$(8.13) \qquad \theta = \epsilon^2 \theta_{(2)} + 0(\epsilon^3) .$$

Since $1 - 2\sigma = k\epsilon^2$, by (2.9) and (4.7) the stress components are

$$(8.14) \qquad T_{ij} = \frac{E}{3k}\theta_{(2)} a_{ij(0)} + 0(\epsilon) ,$$

and the principal part of the stress is a pressure

$$(8.15) \qquad p = -E\theta_{(2)}/(3k) .$$

Using this, (8.11) can be converted into a differential equation for the pressure: it is

$$(8.16) \qquad (\tau^3 a^{\alpha\gamma}_{(0)} p_{,\gamma})_{,\alpha} + \tau^3 F^\alpha_{\alpha\gamma(0)} a^{\gamma\delta}_{(0)} p_{,\delta} - 12k\tau p = 4E\beta^0_{(3)} .$$

If the line-element of S is given by

$$(8.17) \qquad d\eta^2 = b_{\alpha\beta}dx^\alpha dx^\beta = a_{\alpha\beta(0)}dx^\alpha dx^\beta ,$$

then

$$(8.18) \qquad b_{\alpha\beta} = a_{\alpha\beta(0)} , \qquad b^{\alpha\beta} = a^{\alpha\beta}_{(0)} ,$$

and if $G^\alpha_{\beta\gamma}$ are the Christoffel symbols corresponding to $b_{\alpha\beta}$ then

$$(8.19) \qquad G^\alpha_{\beta\gamma} = F^\alpha_{\beta\gamma(0)} .$$

The operation of taking the covariant derivative with respect to $b_{\alpha\beta}$ will be denoted by B_α: also

$$(8.20) \qquad B^\alpha = b^{\alpha\beta}B_\beta ,$$

whence (8.16) can be written in the form

$$(8.21) \qquad B_\alpha(\tau^3 B^\alpha p) - 12k\tau p = 4E\beta^0_{(3)} .$$

These results are summed up as follows:—

VII. For a thin curved membrane of very small compressibility, $1-2\sigma$ being comparable with ϵ^2, the condition that the strain be small and the stress non-infinite requires that the displacement β^i of a point on T be of order ϵ^3 or higher. The principal part of the stress is a pressure p, a function of x^1 and x^2 satisfying the partial differential equation

$$(8.22) \qquad B_\alpha(h^3 B^\alpha p) - 12(1-2\sigma)hp = 4E\beta^0 ,$$

subject to the boundary condition $p = P$ on the edge of the membrane, P being atmospheric pressure. In terms of p the principal parts of the displacement are

$$(8.23) \quad \begin{cases} u^0 = \dfrac{1}{4E}(x^0)^2(3h - 2x^0)B_\alpha B^\alpha p + \dfrac{3}{4E}(x^0)^2(B^\alpha p)(B_\alpha h) - \dfrac{3}{E}(1-2\sigma)x^0 p , \\[2ex] u^\alpha = -\dfrac{3}{2E}x^0(h - x^0)B^\alpha p , \end{cases}$$

and the principal part of the dilatation is

$$(8.24) \qquad \theta = -3(1-2\sigma)p/E .$$

In these formulae x^1 and x^2 are curvilinear co-ordinates on S, x^0 is the length of the normal to S, B^α and B_α are respectively the contravariant and covariant derivatives with respect to the fundamental tensor on S, h is the thickness
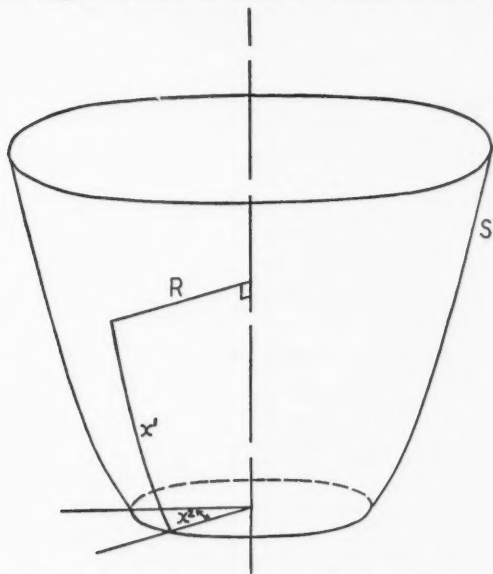

FIG. 3. *System of co-ordinates for the case in which the membrane is attached to surfaces of revolution.*

of the membrane, E is Young's modulus, σ is Poisson's ratio and ϵ is the small parameter defined in (3.1).

The equation (8.22) can also be written in the form

$$(8.25) \qquad \frac{1}{\sqrt{b}}(\sqrt{b}h^3 b^{\alpha\gamma}p_{,\gamma})_{,\alpha} - 12(1-2\sigma)hp = 4E\beta^0,$$

where b is the determinant $|b_{\alpha\beta}|$.

If the surface S is developable it is possible to find a system of surface co-ordinates x^1, x^2 such that the line-element is

$$(8.26) \qquad d\eta^2 = (dx^1)^2 + (dx^2)^2,$$

and for such a co-ordinate system (8.25) becomes

$$(8.27) \qquad (hp_{,\alpha})_\alpha - 12(1-2\sigma)hp = 4E\beta^0.$$

If S is a surface of revolution a co-ordinate system can be chosen in which x^1 is the meridian distance from a standard section normal to the axis of revolution and x^2 is the azimuth (Fig. 3). If R is the radius of a general section normal to the axis of revolution, the line-element will be

$$(8.28) \qquad d\eta^2 = (dx^1)^2 + R^2(dx^2)^2,$$

where R is a function of x^1 only. Then (8.25) takes the form

$$(8.29) \qquad \frac{1}{R}\frac{\partial}{\partial x^1}\left(Rh^3\frac{\partial p}{\partial x^1}\right) + \frac{1}{R^2}\frac{\partial}{\partial x^2}\left(h^3\frac{\partial p}{\partial x^2}\right) - 12(1-2\sigma)hp = 4E\beta^0.$$

9. The Case $n > 2$ (Essential Incompressibility)

In this case the membrane under consideration is less compressible than the periodontal membrane. The condition for finite stress (III) requires that

$$(9.1) \qquad u^0_{(2)} = 0, \qquad \theta_{(1)} = 0, \qquad \beta^i_{(2)} = 0,$$

$$(9.2) \qquad \theta_{(r)} = \frac{\partial u^0_{(r+1)}}{\partial \xi} + u^\alpha_{(r),\alpha} + \sum_{s=0}^{r-2}\frac{1}{s!}\xi^s F^\alpha_{\alpha i(s)}u^i_{(r-s)} = 0,$$

$$(r = 2, 3, \ - \ - \ - \ n-1).$$

Upon making the substitutions indicated in IV it is found that the lowest power of ϵ occurring in (4.13) is ϵ^{n-1} and in (4.14) is ϵ^n, and the corresponding coefficients give rise to the equations

$$(9.3) \qquad \frac{\partial \theta_{(n)}}{\partial \xi} = 0,$$

$$(9.4) \qquad a^{\alpha\gamma}_{(o)}\theta_{(n),\gamma} + k\frac{\partial^2 u^\alpha_{(2)}}{\partial \xi^2} = 0.$$

By a procedure which parallels that in §8 it is found that the principal part of the stress in the membrane is again a pressure satisfying

$$(9.5) \qquad B_\alpha(\tau^3 B^\alpha p) = 4E\beta^0_{(3)}.$$

Since k does not appear in (9.5) it is evident that p does not depend on the compressibility. This means that, when $n > 2$, terms introduced by the assumption of compressibility are negligible in comparison with those retained on the assumption of incompressibility. Hence the term "essential incompressibility" is explained.

Expressed explicitly in the small quantities these results, which are analogous to those in VII, are as follows:—

VIII. For a thin curved membrane of compressibility so small that $1 - 2\sigma$ is comparable with ϵ^n, $(n > 2)$, the condition that the strain be small and the stress non-infinite requires that the displacement β^i of a point on T be of order ϵ^3 or higher. The principal part of the stress is a pressure p, a function of x^1 and x^2 satisfying the partial differential equation

$$(9.6) \qquad B_\alpha(h^3 B^\alpha p) = 4E\beta^0 ,$$

with the boundary condition $p = P$ on the edge of the membrane, P being atmospheric pressure. In terms of p the principal parts of the displacement are

$$(9.7) \qquad \begin{cases} u^0 = \dfrac{1}{4E}(x^0)^2(3h - 2x^0)B_\alpha B^\alpha p + \dfrac{3(x^0)^2}{4E}(B^\alpha p)(B_\alpha h) , \\[2mm] u^\alpha = -\dfrac{3}{2E}x^0(h - x^0)B^\alpha p , \end{cases}$$

and the principal part of the dilatation is

$$(9.8) \qquad \theta = -3(1 - 2\sigma)p/E.$$

In these formulae the notation is as in VII.

It is seen that (9.6) and (9.7) can be derived by putting $1 - 2\sigma = 0$ in (8.22) and (8.23) respectively: (9.6) and (9.7) were also developed by Synge (6, p. 450, equations (56), (57) and (58)).

Acknowledgment

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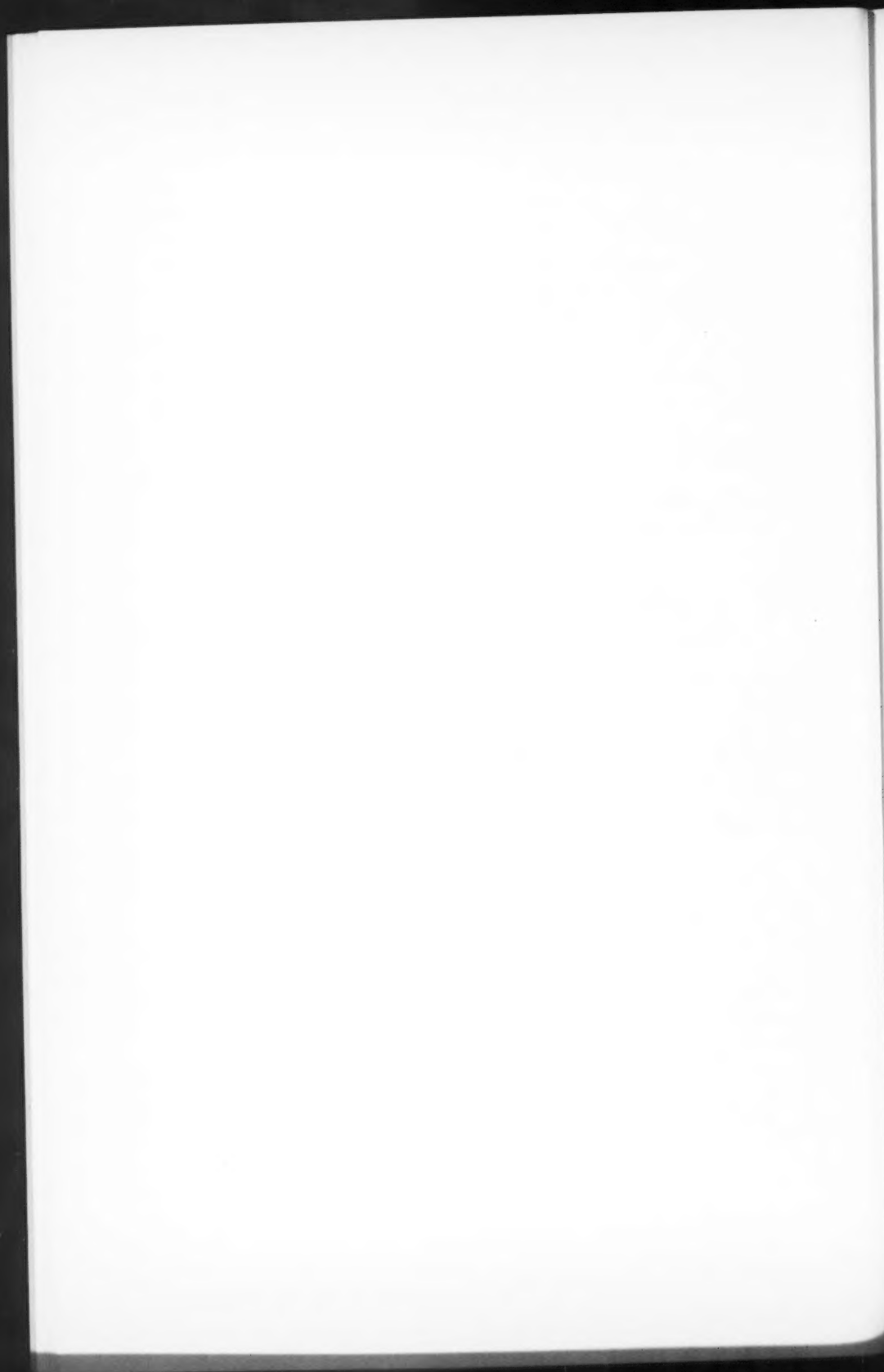
THE PRODUCTION OF ETHANE, QUINHYDRONE, AND POTASSIUM CUPRIC CYANIDE BY A-C. ELECTROLYSIS[1]

BY J. W. SHIPLEY[2] AND M. T. ROGERS[3]

Abstract

The quantitative production of ethane, quinhydrone, and potassium cupric cyanide by a-c. electrolysis was studied in respect to conditions affecting yield. It was found that a good yield (about 90%) of quinhydrone was obtained by a-c. electrolysis, at low frequency and moderately high current density, of an aqueous solution of hydroquinone. This method of preparation has a distinct advantage in respect to space-time yield over the method of d-c. electrolysis. The current yield of potassium cupric cyanide at low current density (0.3 to 1.0 amp. per cm.^{2}) using a.c. was in the neighbourhood of 88%. A-c. electrolysis was not found to indicate any particular advantage over d-c. electrolysis, as far as could be ascertained by comparing the ethane efficiency of the two processes.

Introduction

An investigation by the authors (5) on the electrolysis of some organic compounds by a.c. made it desirable to obtain quantitative data in respect to the conditions affecting the yield of products of certain typical reactions. The reactions chosen were the production of ethane, quinhydrone, and potassium cupric cyanide. It was thought that a study of the conditions affecting yield of product might shed some light on the mechanism of electrolysis and indicate whether a-c. electrolysis might have some specific effect not secured by d.c.

The rate and efficiency of production as a function of current density and frequency were determined, tabulated, and compared graphically.

Experimental

The apparatus for electrolysis and analysis was the same as that described in the preceding paper (5).

THE OXIDATION OF POTASSIUM ACETATE

Potassium acetate was electrolyzed in aqueous solution and in anhydrous acetic acid over a range of current densities. The same concentration of acetate, 50% by weight, was used in all determinations in aqueous solutions and a saturated solution of acetate in anhydrous acetic acid as non-aqueous electrolyte.

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Table I contains the data for the a-c. electrolysis of potassium acetate in aqueous solution. Ethane efficiency is the ratio of the volume of ethane to that of hydrogen produced, while the rate of ethane production is expressed in cc. per min.

TABLE I

OXIDATION OF POTASSIUM ACETATE IN AQUEOUS SOLUTION. TEMP. = 12 TO 15° C.
SOLUTION: 50% POTASSIUM ACETATE, 5% ACETIC ACID

Current density, amp. per cm.^{2}	H_2, %	O_2, %	C_2H_6, %	Rate of evolution of C_2H_6, cc. per min.	Ethane efficiency, %
1	58.8	0.2	10.0	0.2	17.0
2	57.0	0.0	16.2	3.2	27.5
3	53.5	0.0	21.8	6.6	40.7
4	51.9	0.0	23.0	10.0	44.3
5	49.2	1.0	25.8	15.2	52.4
6	48.0	1.3	26.7	20.7	55.6
7	40.0	2.0	24.8	27.3	62.0
8	52.2	2.0	33.0	33.0	63.3

Table II gives the data for the a-c. electrolysis of potassium acetate in anhydrous acetic acid.

TABLE II

ELECTROLYSIS OF POTASSIUM ACETATE IN ANHYDROUS ACETIC ACID. TEMP. = 25° C.
ELECTRODES, SMOOTH PLATINUM

Current density, amp. per cm.^{2}	Rate of gas evolution, cc. per min.	H_2, %	C_2H_6, %	Rate of evolution, of C_2H_6, cc. per min.	Ethane efficiency, %
0.57	0.30	43.7	13.4	0.04	
1.0	3.1	36.1	21.5	0.62	59.6
1.2	6.4	33.7	23.2	1.5	68.8
1.5	8.0	35.6	26.0	2.08	73.0
1.9	9.4			2.45	
2.5	22.6	33.8	25.7	5.8	76.0
3.2	40.0	31.3	24.7	9.88	79.0
3.5	47.0			11.7	

Because of the high resistance of the electrolyte higher currents could not be used.

OXIDATION OF HYDROQUINONE

(a) A saturated solution of hydroquinone in water at 0° C. was used. About 30 cc. of 6 N sulphuric acid was added per litre to make the solution conducting. The electrolytic solution was cooled in ice, and platinum wire electrodes were used. The quinhydrone was obtained by cooling the solution to 0° C., at which temperature it is very slightly soluble, filtering off the precipitate on a tared filter, washing with water, drying, and weighing. This was repeated over the range of current densities from the decomposition point of 0.5 amp. per cm.^{2} to 10 amp. per cm.^{2}

A series of determinations was also made at frequencies of 20 and 30 cycles at current densities up to 6 amp. per cm.[2]

These frequencies were obtained by means of a Westinghouse motor-generator set using a separately excited armature and field. The frequency was calculated from the speed of the generator.

(b) The procedure of *(a)* was repeated using gold electrodes prepared by plating platinum with gold.

(c) Corresponding data were obtained using d.c.

The data are collected in Tables III to VI.

TABLE III

ELECTROLYSIS OF HYDROQUINONE

Electrodes, smooth platinum.   Frequency, 60 cycles

Current density, amp. per cm.[2]	Yield of quinhydrone, gm. per min.	Rate of gas evolution, cc. per min.	CO_2, %	O_2, %	O_2, cc. per min.	Amp. per min. used to produce O_2
0.03	0.0045					
0.5	0.0008					
1	0.01	3.0	0.3	1.2		
2	0.03	5.6				
3	0.08	11.3	0.3	1.3	0.14	0.04
4	0.15	16.3	0.5	1.6	0.25	0.07
5	0.20	23.5				
6	0.26	32.2	0.6	1.8	0.58	0.10
7	0.35	39.0	0.8	2.0	0.78	0.40
8	0.38	45.5	1.3	2.8	1.23	0.50
9	0.41	54.6	1.3	4.8	2.60	0.73
10	0.45	58.8	1.0	6.0	3.53	1.0

TABLE IV

ELECTROLYSIS OF HYDROQUINONE

Gold electrodes.   Frequency, 60 cycles

Current density, amp. per cm.[2]	Yield of quinhydrone, gm. per min.	Rate of gas evolution, cc. per min.	CO_2, %	O_2, %	O_2, cc. per min.	Amp. per min. used to produce O_2
1		1.6				
1.2	0.009					
2	0.040		0.4	0.6		
2.5	0.070					
3	0.112	12.05	0.0	2.0	0.25	0.07
3.5	0.163				0.54	
4	0.185	18	0.1	3.0	0.54	0.15
4.5	0.216					
5	0.230	25.6	0.3	3.8	0.97	0.27
6	0.265	29.5	0.7	4.8	1.41	0.40
7	0.315	40.0	1.1	6.0	2.40	0.67
8	0.370	46.2	1.5	6.5	3.0	0.84
9	0.410	55.2	2.0	8.1	4.5	1.26
10	0.450					

TABLE V

ELECTROLYSIS OF HYDROQUINONE.   DIRECT CURRENT

Current density, amp. per cm.^{2}	Yield of quinhydrone, gm. per min.	
	Platinum electrodes	Gold electrodes
0.15	0.006	
1	0.06	
2	0.106	0.12
4	0.21	0.22
5		0.27
6	0.35	0.32
7	0.39	0.37
8	0.42	0.41
9	0.44	0.44
10	0.45	0.50

TABLE VI

ELECTROLYSIS OF HYDROQUINONE WITH DIFFERENT ELECTRODES AND FREQUENCIES

Current density, amp. per cm.^{2}	Yield of quinhydrone, gm. per min.		
	Au electrodes, 20 cycles	Pt electrodes, 30 cycles	Pt electrodes, 20 cycles
0.5			0.011
1	0.041	0.025	
1.5			0.07
2		0.085	
2.5		0.115	0.13
3	0.165		
3.3			0.18
3.87		0.190	
4.5		0.235	0.26
5	0.285		
5.5			0.285
6	0.356		
7			0.31

It is seen from the above that decrease in frequency increases the yield, and that gold electrodes give a slightly better yield than platinum.

Influence of Other Factors on Yield of Quinhydrone

Effect of Added Ions

Various ions which might act as oxygen carriers were added, *e.g.*, CrO_4^{--}, Mn^{++}. They caused no change in the yields.   Ions such as Na^+ and Ca^{++}, had no effect.

Influence of Temperature

Below 40° C., temperature was found to have but a slight effect on yield. Above 40° C., a distinct lowering of yield occurred with rise in temperature.

Influence of Electrode Material

The results for gold and platinum are in general similar. Gold gives a slightly higher yield over the range 0 to 5 amp. per cm.^{2} at 60 cycles, but at 20 cycles the yields are nearly the same. Silver, nickel, and iron electrodes dissolve in the solution, and no quinhydrone is formed. Carbon is quite efficient, the yields being comparable to those given by gold and platinum. Owing to the difficulty of determining surface area exactly, comparison is impracticable.

Influence of Acid Concentration

The concentration of sulphuric acid was found to have but a small effect on yield at 25° C. However, low concentrations give a high resistance electrolyte, and the resultant heating lowers the yield.

Phase Difference

To determine whether capacitance had any effect on the phase relations of current and e.m.f., an oscillograph was connected in the circuit. At all frequencies (60 cycles and lower) and current densities (0.5 amp. per cm.^{2} and higher) used there was no phase angle.

Decomposition Potentials

A cell containing 40% potassium acetate solution in water with 1% acetic acid was used at 20° C. Platinum electrodes were introduced as previously described. These gave a uniform current density and their area was known. The potential was slowly raised and the current and potential at the decomposition point observed, this point being taken as that at which bubbles of gas were first evolved continuously. After some time the electrolyte became warm and platinum black formed. The evolution then ceased, and increasing potentials were required to evolve gas. There was therefore no definite reproducible value of decomposition potential. With 50% potassium acetate and 0.7 volts the first evolution of gas occurred at a current density of 0.27 amp. per cm.^{2} This gives the intercept of the ethane-evolution curve on the current axis (see Fig. 1).

With a saturated solution of potassium acetate in glacial acetic acid the current density at which bubbles are first continuously evolved is 0.31 amp. per cm.^{2}. This gives the intercept on the current density axis in Fig. 1. For the determination of the potential at which quinhydrone is first formed, a saturated solution of hydroquinone in 0.1 M sulphuric acid was used. The first crystals of quinhydrone were observed at a potential of 1.2 volts and a current density of 1.35 amp. per cm.^{2} With d.c., 0.67 volts is the potential at which quinhydrone forms first.

The values of current plotted against potential gave, in all cases observed, a curve without a sharp break such as is noted with d.c. There appears to be no a-c. analogue of the d-c. decomposition potential.

Figs. 1, 2, 3, and 4 show the relation of rate of production with a-c. electrolysis to that required by Faraday's law.
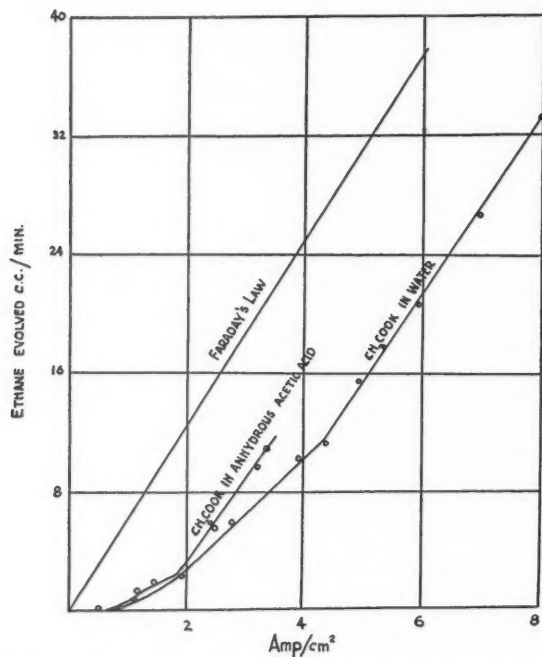
FIG. 1.   *The rate of production of ethane from potassium acetate at platinum electrodes.*
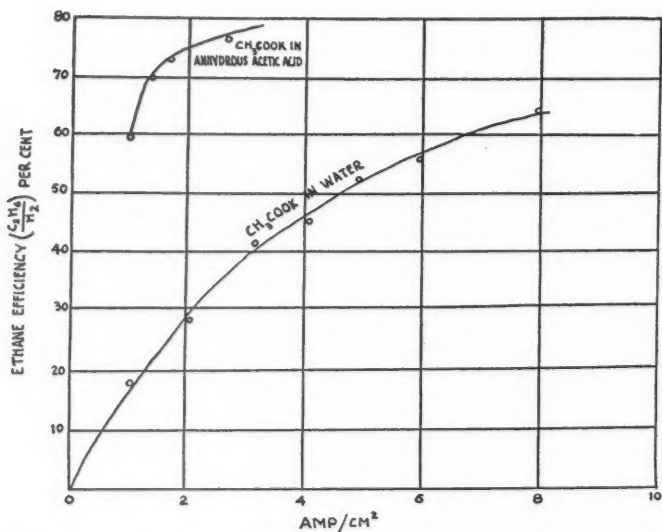
FIG. 2.   *The variation of the efficiency of ethane production with current density.*

THE INFLUENCE OF CURRENT DENSITY ON THE SOLUTION OF COPPER ELECTRODES IN POTASSIUM CYANIDE

In order to obtain some knowledge concerning a reaction in which the formation of a complex ion is the irreversible process in electrolysis, the formation of potassium cupric cyanide by the a-c. electrolysis of an aqueous solution of potassium cyanide was studied, copper electrodes being used.
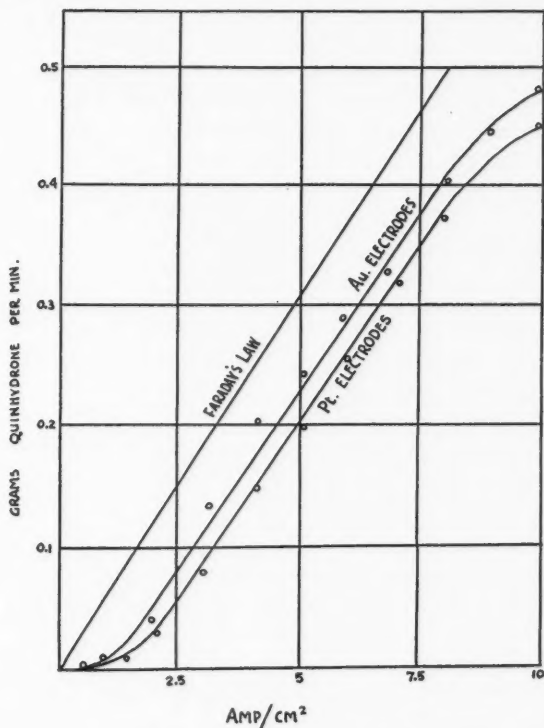

FIG. 3. *The rate of production of quinhydrone at platinum and gold electrodes with 60 cycle a.c.*

The reaction

$$2Cu + 8KCN + 2H_2O + 2e \longrightarrow 2K_3Cu(CN)_4 + 2KOH + H_2$$

takes place with a.c. since the copper ions first formed are removed as the complex cyanide, from which they are electrolytically deposited only with difficulty (2).

The influence of current density on this reaction was determined by passing an a.c. between weighed copper electrodes in 4 N potassium cyanide solution. After a known quantity of electricity had passed, the electrodes were dried and weighed. The current efficiency of the reaction for the solution of copper

was calculated from the loss in weight of the electrodes. The results are shown in Table VII.

TABLE VII

CURRENT EFFICIENCY

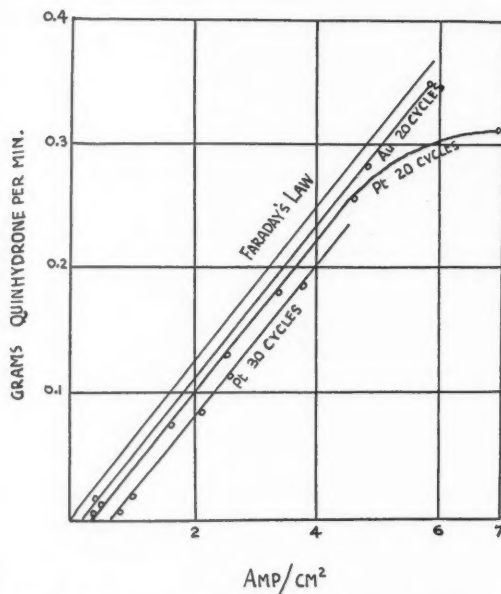| Current density, amp. per cm.²	0.05	0.3	0.7	1.0	1.75	2.0	3.0
Current efficiency of process, %	84.1	89.2	87.2	88.2	66.6	38.0	30.8

FIG. 4. *The rate of production of quinhydrone at platinum electrodes at frequencies of 20 and 30 cycles, and at gold electrodes at 20 cycles.*

No carbon dioxide was evolved and the percentage of oxygen was always less than 1. Thus, up to a value of 1 amp. per cm.² the current density has little effect on current efficiency. At current densities higher than this the efficiency decreases rapidly. It may be assumed that at high current density the number of copper ions formed is greater than the number that can be removed as complexes in the time before the sign of potential of the electrode changes. The copper ions so remaining will be at once reduced to copper when the electrode becomes cathode. If the copper ions are not removed when the electrode becomes cathode, the copper will be electrolytically deposited. The reaction above is of a nature different from that of the reactions previously considered. This reaction is independent of current density until high current densities are reached, when copper ions are supplied more rapidly than they can be removed.

The results with iron electrodes were similar to those obtained with copper. Stirring was found to increase the yield at high current densities, a result expected from the above theory, and therefore confirming it.

Discussion

The three electrolyses studied in detail gave the same general results. At low current densities (below 0.5 amp. per cm.[2]) the yield of products was very small. The best yields with d.c. are usually obtained at current densities lower than the above value. A-c. electrolysis apparently gives a relatively rapidly increasing yield of products over a range of current densities from the decomposition potential up to the point at which the rate of increase is in conformity with Faraday's law (see Fig. 3). It will be seen from this figure that, although the yield of products in this range is in conformity with that required by Faraday's law, they differ by a constant value. Thus, above a certain definite current density [critical current density—(3, 4, p. 3)], all additional current produces electrolytic products at a rate in accordance with Faraday's law.

This suggests that some constant factor, such as the capacity of the electrodes to hold electrolytic products, must be involved in the a-c. electrolysis of organic compounds.

Fig. 1 shows that after a current density of 4 amp. per cm.[2] was reached the production of ethane became progressively greater with increase in current density in accordance with that required by Faraday's law. This indicated that the capacity of the electrodes for holding electrolytic products has become constant, and that electrolysis is proceeding as though but one determinate reaction was occurring. If more than one electrolytic reaction influencing the production of ethane were taking place, it could not be expected that this rate would be parallel with the rate of production required by Faraday's law.

In the case of potassium acetate in anhydrous acetic acid the only theory to account for the production of ethane is the discharged ion theory of Brown and Walker (1), and no chemical oxidation can occur. According to this theory the acetate ions are discharged at the anode; two free radicals then combine and decompose to give the products:

$$2CH_3COO^- \longrightarrow 2CH_3 . COO + 2e$$
$$2CH_3COO \longrightarrow C_2H_6 + 2CO_2 .$$
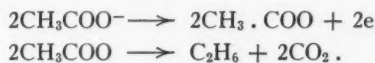
If the mechanism of electrolysis is of this nature, it might be expected that, since the discharged radicals take a finite time to decompose, some may not have decomposed when the current reverses. When the electrode becomes cathode, electrons are supplied and the radical would take up an electron. This would correspond to a decreased yield of ethane. The electrode would at the same time absorb hydrogen formed by discharge of hydrogen ions. On reversal of the current this hydrogen would be removed by oxidation or by the reverse process to give hydrogen.

$$H_2 \rightleftarrows 2H \qquad\qquad H \rightleftarrows H^+ + e.$$

At current densities greater than 2 amp. per cm.² the curve for potassium acetate in anhydrous acetic acid (Fig. 1) becomes parallel to that required by Faraday's law, but is displaced from it by a constant current density. This indicates that the ratio of the current, represented by the sum of the current used to remove hydrogen absorbed on the electrode plus that used by a discharged radical in again taking up an electron, to the current represented by a half-wave of a-c. current, has become constant. The curve for ethane production therefore is parallel to that required by Faraday's law at current densities above 2 amp. per cm.² The curves for hydrogen and oxygen production by the a-c. electrolysis of water (3, p. 325), were also found to depart in a similar manner from those required by Faraday's law. This was accounted for by assuming that the storage capacity of the electrodes for electrolytic gases decreased with the area of the half-wave below a certain current density. If this is the explanation of the observed curvature at low current densities, the same explanation applies to the curvature, at low current densities, of all the curves in Figs. 1, 3 and 4. It is obvious that a lower storage capacity for electrolytic products on the electrodes will leave a greater proportion of the total quantity of electricity in the half-wave available for the oxidation and reduction of the depolarizer (organic or inorganic).

The curves for the oxidation of hydroquinone in Fig. 3 are similar to the curves for ethane production included in Fig. 1, except that at high current densities the curves depart from parallelism with Faraday's law. It was found from the gas analysis data in Table I that oxygen evolution increased rapidly at high current density, and that this increase corresponded to the increase of curvature in the quinhydrone production curves of Fig. 3. This indicates that oxygen evolution partly replaces oxidation of hydroquinone to quinhydrone at high current density. Complete oxidation of hydroquinone did not occur to any appreciable extent, as shown by the absence of maleic acid in the analysis, and therefore the curvature was not due to complete oxidation of the benzene ring. At current densities above 7 amp. per cm.², the percentage of carbon dioxide in the gas evolved indicates that some complete oxidation had occurred.

The portion of the quinhydrone production curve parallel to that required by Faraday's law indicates that over this range of current densities the storage capacity of the electrodes for hydrogen and oxygen (3, 4, p. 3) is similar to that in the a-c. electrolysis of water. At high current densities it is probable that the storage capacity of the electrodes for hydrogen and oxygen remains unchanged, but hydroquinone does not diffuse to the electrode rapidly enough to accept all the oxygen produced by the discharge of the hydroxyl radical, and therefore oxygen is evolved.

The area of the half-wave representing a.c. decreases with increasing frequency. The ratio of the current not used in the oxidation of hydroquinone (owing to the capacity of the electrode for storing hydrogen and oxygen) to the total current passing, represented by the half-wave, will increase with

increasing frequency (3, p. 317). Therefore the yield of quinhydrone at low frequencies will be greater, as was found experimentally.

The portion of the production curves which parallels those given by Faraday's law gives a measure of the yield to be expected as a function of current density. It is probable that a study of other a-c. electrolytic reactions might show but a short range where this parallelism occurs, and significant yields as a function of current density would not be indicated. At very high current densities the depolarizer could not be supplied to the electrode rapidly enough, and oxygen and hydrogen evolution from aqueous solutions, and alternative oxidation and reduction processes when organic solvents are used, would occur. For example, when the acetate ion cannot be supplied rapidly enough to the electrode, oxidation of acetic acid to methanol may occur rather than the Kolbe synthesis producing ethane.

Current yields of quinhydrone greater than 90% were obtained at low frequencies and moderately high current densities. Corresponding yields with d.c. were obtained only at very low current densities. Thus the a-c. production of quinhydrone would be found advantageous in respect to space-time yield. The possible advantage of a-c. production over d-c. is that the high yields are obtained at high current densities. Also, the alternation of current favours the diffusion of depolarizer to the electrode surface, and tends to give a higher current efficiency for the products.

An indeterminate factor in a-c. electrolysis is the effect of local heating on the electrode surface.

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FURTHER OBSERVATIONS ON THE DETERMINATION OF PHOSPHATE BY PHOTOELECTRIC COLORIMETRY[1]

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Abstract

A study of factors affecting the ceruleomolybdate reaction for phosphate is reported. The concentrations of stannous and stannic ions, the presence of extraneous salts, and temperature are important factors affecting the intensity and stability of the blue colour.

The stannous chloride reagent should be preserved from oxidation by storing it under hydrogen.

The interference by ferric iron is due largely to its reaction with the reducing agent, and may be avoided by diluting the sample to contain 0.1 p.p.m. of phosphorus and using two or three times the usual quantity of stannous chloride.

The method for the determination of phosphate recently described (3) in a communication from this laboratory has been in constant use since that time in studies of soil phosphorus relationships. Certain difficulties have been encountered which have led to further investigation of the factors influencing the development and stability of the ceruleomolybdate colour. This article is intended to amend and supplement certain of the data reported in the previous paper.

Effect of Stannous and Stannic Ions

In the earlier work the recommendations of Truog and Meyer (9) with regard to the concentrations of the reagents were adopted. The effect of stannous chloride was investigated (3) on the unwarranted assumption that the stannous chloride used to prepare the 2.5% reagent was pure. The use of a new lot of stannous chloride in the preparation of the reagent resulted in a considerable increase in the calibration constant, and also gave an appreciable colour in the control solutions. Analysis of the two lots of stannous chloride by iodimetric titration, according to Scott (6), but without reduction of the stannic ion, showed only 32.4% of stannous tin in the old sample, as compared to 93.8% stannous tin in the new sample. In terms of a 2.5% solution of stannous chloride the effective concentrations were 0.81 and 2.37% respectively.

The effect of the new stannous chloride on the rate and extent of colour development was investigated. Different amounts of stannous chloride, as indicated in Table I, were added to 10 ml. aliquots of phosphate solutions containing acid molybdate, and the colour development was followed by means of the Evelyn colorimeter. A series of results is given in Fig. 1. The curves show that the concentration of stannous ion exerts a very considerable influence
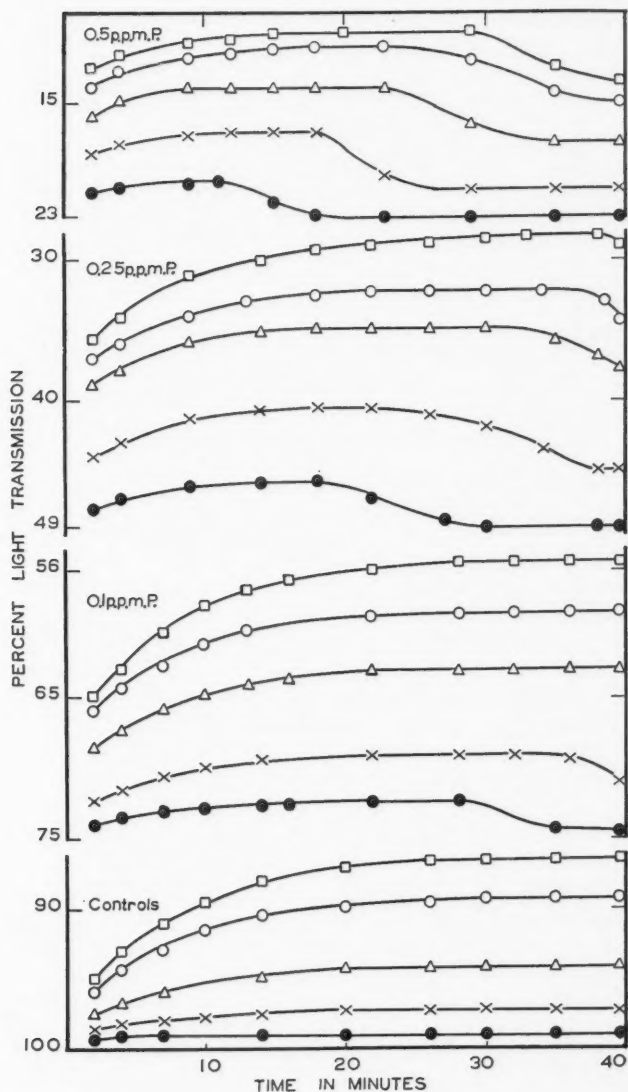
FIG. 1.   *The influence of stannous chloride on the development and stability of the blue colour.*
● *1 drop of 1% SnCl₂ . 2H₂O;* × *1 drop of 2% SnCl₂ . 2H₂O;* △ *1 drop of 3% SnCl₂ . 2H₂O;*
○ *1 drop of 4% SnCl₂ . 2H₂O;* □ *1 drop of 5% SnCl₂ . 2H₂O.   (21 drops equal 1 cc.; temperature of all solutions, 23.5° C.)*

on the colour development, since an increase in its amount results in an increase in the maximum colour intensity, and also increases the time required before the maximum is reached, and the length of time for which the colour
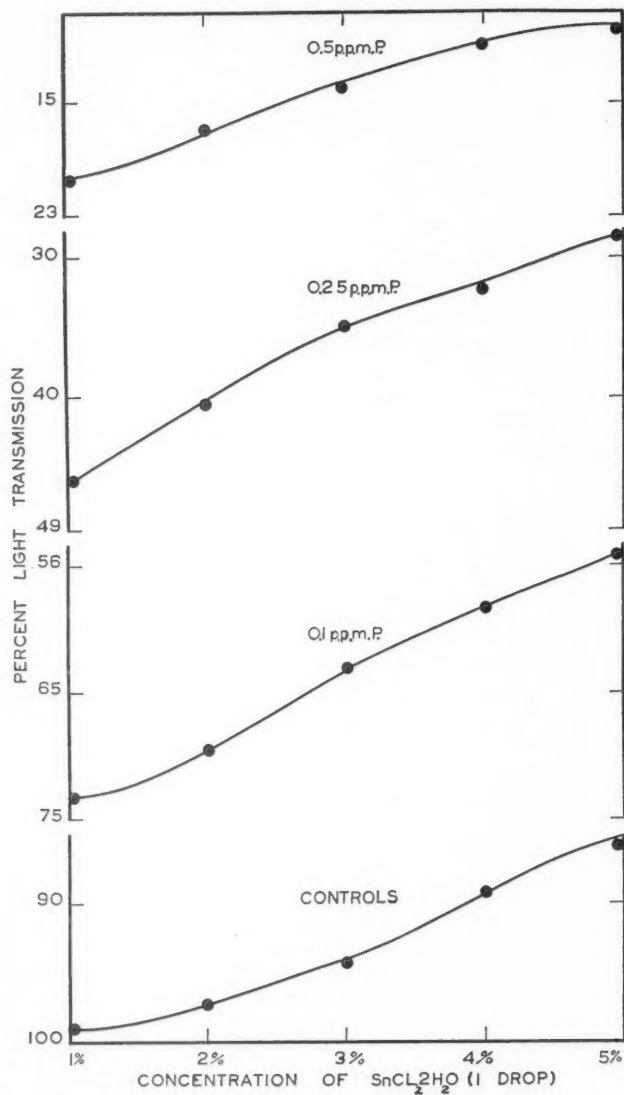

FIG. 2.   *The effect of stannous chloride on the maximum colour intensity.   (Temperature of all solutions, 23.5° C.)*

is stable. This influence of stannous chloride is due in part to the development of appreciable colour in the control solutions. The reaction involving phosphate is also affected since the K_1 values distinctly increase with increasing concentrations of stannous chloride even when correction is made for the control solution (see Table I).

TABLE I

EFFECT OF INCREASING AMOUNTS OF STANNOUS CHLORIDE ON THE CALIBRATION CONSTANT
(TEMPERATURE OF ALL SOLUTIONS, 23.5° C.)

SnCl$_2$. 2H$_2$O	Value of K_1		
	0.1 p.p.m. P	0.25 p.p.m. P	0.5 p.p.m. P
1 drop of 1% SnCl$_2$. 2H$_2$O	1.35	1.33	1.34
1 drop of 2% SnCl$_2$. 2H$_2$O	1.48	1.52	1.51
1 drop of 3% SnCl$_2$. 2H$_2$O	1.74	1.72	1.65
1 drop of 4% SnCl$_2$. 2H$_2$O	1.78	1.78	1.81
1 drop of 5% SnCl$_2$. 2H$_2$O	1.94	1.94	1.88

Fig. 2, showing the effect of stannous chloride on the maximum colour intensity, is intended to supersede the same figure of the earlier paper (3), as it shows better the effects of different amounts of stannous chloride on colour development.

The data in Fig. 1 show quite different rates of colour development and fading than were previously observed [(3), Fig. 3]. With the new sample of stannous chloride the colour developed more slowly, and for a given amount of phosphorus was finally more intense and more stable than with the old sample, even when the comparison was made with equal additions of stannous ion. From this standpoint the main difference between the two reagents would be the greater proportion of stannic ion in the old preparation. According to Hein, Burawoy and Schwedler (4), stannic ion influences the reaction equilibrium.

An experiment was carried out to test the hypothesis that the difference in the action of the two samples of stannous chloride was due to their content of stannic ion. To aliquots of a phosphate solution were added varying amounts of a 2.5% solution of stannic chloride and the usual reagents. The results are shown in Fig. 3. Stannic ion causes the fading to take place sooner, and, in higher concentration, inhibits the maximum colour development. These results would then appear to explain why the two solutions of stannous chloride should result in different behaviour even when compared on the basis of equal concentrations of stannous ion. Probably no two samples of stannous chloride will give identical results. Consequently, whenever new stannous chloride reagent is employed it is necessary that a new calibration be made, and the time required for maximum colour development determined.

In the technique used, the galvanometer was adjusted to give a reading of 100, corresponding to maximum scale deflection, before addition of the stannous chloride, in order to compensate for any colour in the soil extract. Such

a procedure is a satisfactory basis of comparison only if no blue colour develops
in a phosphate-free solution.   The results shown in Figs. 1 and 2 indicate
that one drop of 1% stannous chloride reagent is about the maximum that
can be added to each tube without the production of an appreciable colour
in the control solution.   This condition is satisfied if the stannous chloride
solution is prepared in the following manner:— Dissolve 10 gm. of stannous
chloride in 100 ml. of 6N hydrochloric acid (redistilled) and dilute to 500 ml.
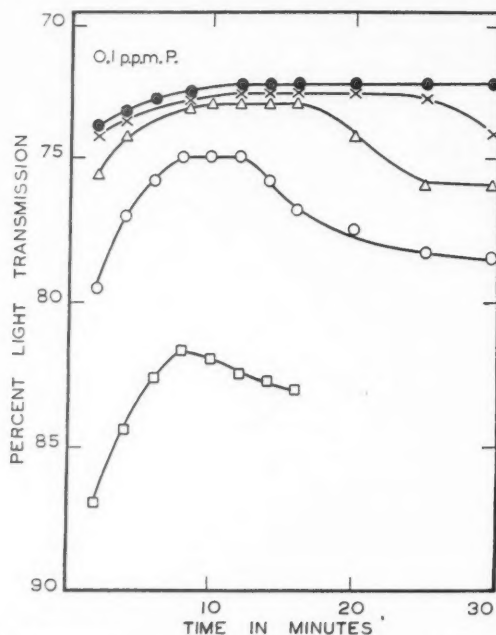with recently boiled distilled water.   Titrate aliquots by the iodometric

FIG. 3.   *The influence of stannic ions on the colour development and fading.*   ● *No* $SnCl_4$;
× *1 drop of* $SnCl_4$; △ *3 drops of* $SnCl_4$; ○ *6 drops of* $SnCl_4$; □ *10 drops of* $SnCl_4$.   *(Tem-
perature of all solutions, 24° C.; 21 drops equal 1 cc.; 1 drop of 1%* $SnCl_2$. $2H_2O$ *used in all
solutions.)*

method of Scott (6) omitting the reduction of stannic ion, and calculate the
true content of stannous chloride.   Dilute to 1% with 1.2 N redistilled hydro-
chloric acid and store under hydrogen.   If this is done the usual procedure of
adding one drop of the reagent to each tube may be followed and the colour in
the control solution will be small enough to ignore.   However, larger amounts
of stannous chloride may be used, provided that a correction is made for the
colour developed in the control solution.   A typical calculation is given
below.   Suppose the galvanometer deflection for the control is 90.   Then a
reading of 50 for an unknown represents a percentage light transmission of
$\frac{50 \times 100}{90}$.

Deterioration of Stannous Chloride Reagent

In view of the effect of stannous and stannic ions on the colour development, the stability of the stannous chloride reagent is important. Oxidation will tend to lessen the stability of the colour, and to diminish the calibration constant.

Since stannous chloride, both in the solid form and in solution, is oxidized when exposed to the atmosphere, some precaution must be taken to minimize this change. The recommendation of Truog and Meyer (9) that the surface of the solution be covered with a layer of mineral oil to retard oxidation appears to have been generally adopted. However, even under oil a considerable deterioration goes on. It was observed that 10% of the stannous ion in a 1% solution of stannous chloride was oxidized in two weeks, even when protected in this manner.

The apparatus used by Sutton (7) to prevent the oxidation of titanous chloride proved to be very effective for the preservation of the stannous chloride reagent. The method consists in storing the solution under hydrogen, supplied by a small automatic generator which is connected in a closed system with the stannous chloride bottle. No deterioration of the reagent could be detected after more than a month of storage under hydrogen.

Effect of Chloride

It is well known that the common inorganic anions, when present in sufficient amounts, affect the course of the ceruleomolybdate reaction. According to Chapman (2) sulphates intensify the colour, nitrates have little or no effect on the colour maximum but induce an earlier, more pronounced fading, while chlorides reduce the colour maximum and cause earlier fading.

The action of chloride was studied because it was of interest in connection with a method for determining organic phosphorus, details of which will appear elsewhere in this Journal. Some of the data on this effect are shown in Fig. 4. The action of ammonium chloride in decreasing the colour development and causing early fading is evident. Further, it has been observed that the effect of sodium chloride is almost identical with that of ammonium chloride, so the action seems to be entirely due to the chloride ion.

These results illustrate the magnitude of the errors that may occur through overlooking the action of dissolved salts. For accurate visual colorimetry, it is necessary that the standard be made to contain an equal concentration of the salts that are present in the unknown with which it is to be compared. Similarly, in the photoelectric method, the calibration constant that is applicable to an unknown solution must be determined from the colour intensity developed in a standard phosphate solution containing equal concentrations of the ions that affect the reading.

The results obtained here indicate that the calibration constant is affected to about the same extent at different phosphate levels by a given, moderate salt concentration. In the ordinary instance, where a known amount of

chloride or sulphate has been produced in a solution by neutralization, it is a simple matter to obtain a valid calibration constant, and so avoid appreciable errors.   If, however, the chloride concentration is so great as to cause early fading it is rather difficult to obtain accurate results.
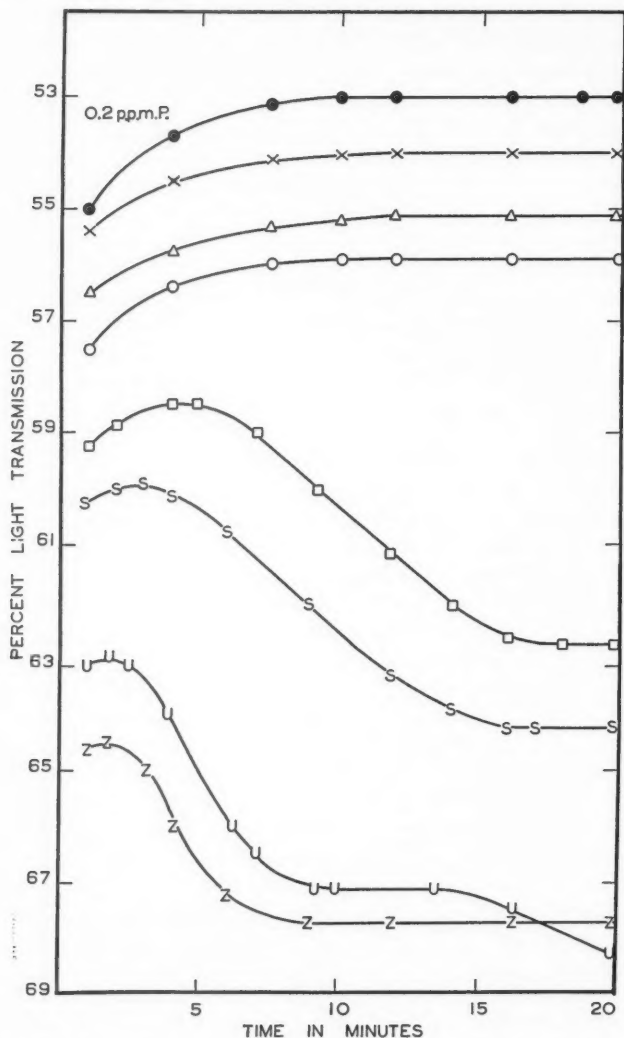

FIG. 4.   *The effect of chloride concentration on colour intensity and fading.*   ● *No chloride ion.*   × *700 p.p.m. chloride ion;* △ *1400 p.p.m. chloride ion;* ○ *3500 p.p.m. chloride ion;* □ *9300 p.p.m. chloride ion;* S *18,600 p.p.m. chloride ion;* U *37,200 p.p.m. chloride ion;* Z *46,500 p.p.m. chloride ion.   (Temperature of all solutions, 21° C.)*

Effect of Temperature

Occasionally, but particularly during the spring and summer months, seemingly unaccountable variations of the calibration constant have been observed.   A study of the conditions associated with these aberrations led to the belief that temperature fluctuations might be responsible for the trouble.
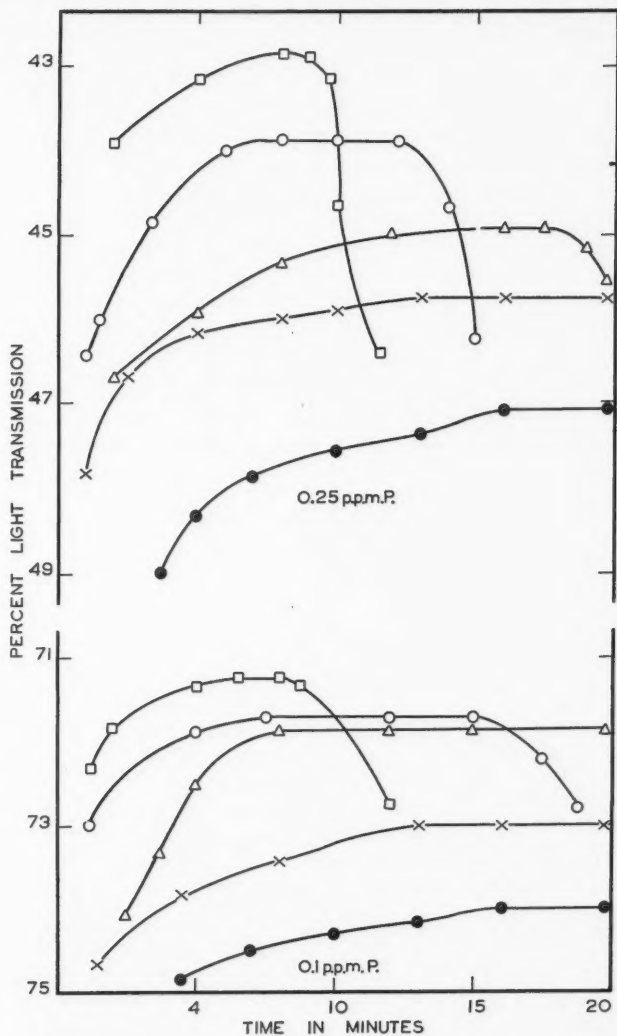

FIG. 5.   *The influence of temperature on the development and stability of the colour.*
● *15° C.;* × *20° C.;* △ *24° C.;* ○ *28° C.;* □ *35° C.   (1 drop of 1% SnCl₂ . 2H₂O used to develop colour in all solutions.)*

As was noted previously (3), temperature exerts an effect on the intensity of the blue colour.   More definite information on the nature and extent of this effect was sought.   Fig. 5 shows curves obtained by following the colour development in two different phosphate solutions at several temperatures that cover the range of probable working conditions.   The colorimeter tubes were placed in small water baths adjusted to the desired temperatures throughout the course of the reaction, and removed at intervals for the short time required to take a reading.   Although the temperature might have changed slightly during the time when the readings were made, the results show clearly enough that the prevailing temperature exerts a significant effect on the colour development, and hence calibration data are strictly valid only for the temperature at which they were obtained.   An increase in temperature results in an increase in the maximum colour development, and also in the reaction rate, as indicated by more rapid colour development, and decreased stability. The results indicate that it would be desirable to carry out the determinations under constant temperature conditions.   Failing this, it has proved quite satisfactory in practice to include a standard phosphate solution in each set of determinations, and thus to establish the appropriate K_1 value to use with that set.

Table II records the values of K_1 corresponding to the maximum colour development at each temperature studied.   It is clear that the effect of temperature on the calibration constant is the same at both phosphate levels.

TABLE II

THE EFFECT OF TEMPERATURE ON THE CALIBRATION
CONSTANT

Temperature, °C.	Value of K_1	
	0.1 p.p.m. of P	0.25 p.p.m. of P
15	1.31	1.30
20	1.37	1.35
22	1.43	1.39
24	1.43	1.39
26	1.44	1.43
28	1.44	1.43
30	1.46	1.47
35	1.47	1.48

Effect of Ferric Iron

In the course of some recent determinations of the phosphorus content of soil colloids, it was observed that much higher values of phosphorus were obtained for diluted portions than for the original extract.   Similar behaviour was attributed by Holman and Pollard (5) to an interference caused by dissolved organic matter.   However, in the present instance it is certain that the effect was not due to organic matter, as ignition did not eliminate the interference.

The colour development and fading were studied in soil extracts that showed this behaviour. Typical results are shown in Fig. 6. It is evident that in the more concentrated solutions the colour develops rapidly and fades almost
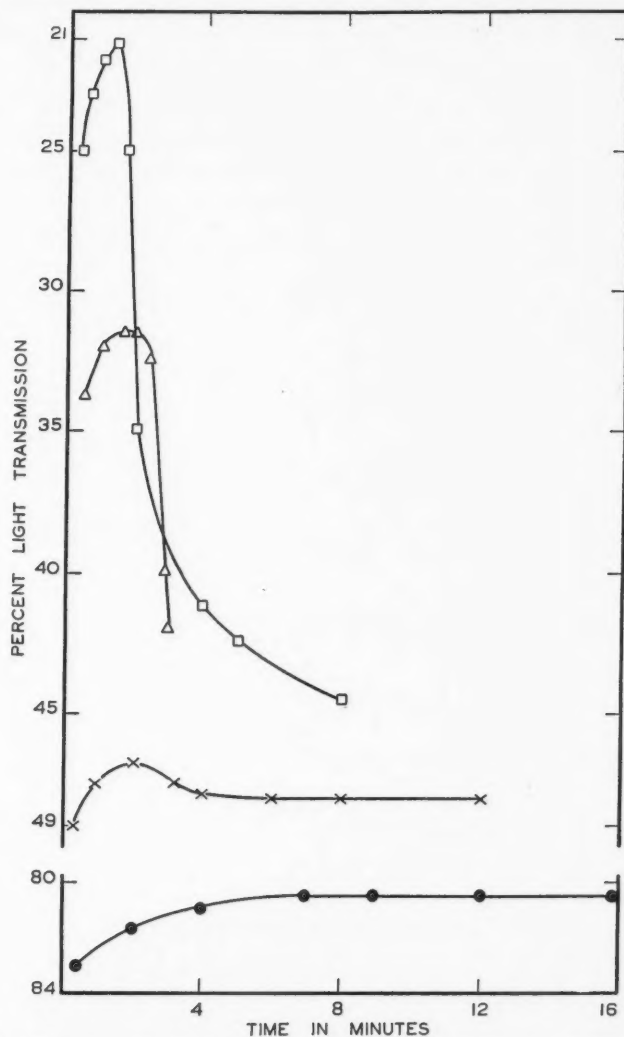

FIG. 6. *The nature of the interference due to iron observed in soil extracts.* ● *Acid extract before ignition. Dilution 1 to 10,000. Diluted extract contained 3 p.p.m. iron and 0.07 p.p.m. phosphorus.* × *Acid extract before ignition. Dilution, 1 to 2860. Diluted extract contained 10.5 p.p.m. iron and 0.24 p.p.m. phosphorus.* △ *Acid extract before ignition. Dilution, 1 to 2000. Diluted extract contained 15 p.p.m. iron and 0.34 p.p.m. phosphorus.* □ *Acid extract after ignition. Dilution, 1 to 2000. Diluted extract contained 15 p.p.m. iron and 0.54 p.p.m. phosphorus.* (*Temperature of all solutions, 24° C.*)

immediately, so that there is a sharp colour maximum within the first three minutes.   Readings made five minutes after the addition of stannous chloride indicate much less than the maximum colour development.   On dilution of the original solution in successive stages this sharp rise to a maximum is less apparent and is finally absent.   The effect was observed to be the same in the ignited extracts as in those where organic matter was present.

Analyses showed that the solutions which exhibited this behaviour contained ferric iron in considerable concentrations.   The interference of ferric iron was then studied in an attempt to account for the observed results.   The colour development and fading were traced in phosphate solutions containing various known concentrations of ferric iron.   The data obtained are reproduced graphically in Fig. 7.   At the phosphorus concentration used in this experiment, 0.2 p.p.m., the effect of 1.0 p.p.m. of iron is negligible, but all
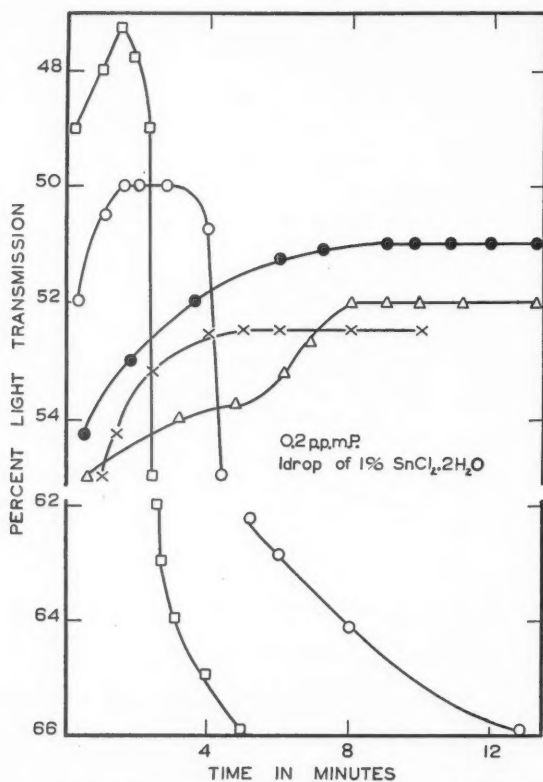

FIG. 7.   *The influence of ferric iron concentration on the behaviour of the colour, using one drop of 1% stannous chloride reagent.   ● No ferric iron; × 5 p.p.m. of ferric iron; △ 10 p.p.m. of ferric iron; ○ 20 p.p.m. of ferric iron; □ 35 p.p.m. of ferric iron.   (21 drops equal 1 cc.; temperature of all solutions, 24° C.)*

the higher concentrations of iron cause appreciable errors.   Thus, 2, 5, and 10 p.p.m. of iron prevent the normal colour development, whereas 20 and 35 p.p.m. of iron result in a rapid rise to an abnormal maximum, followed by early and rapid fading.   It has also been observed that when the phosphorus con-
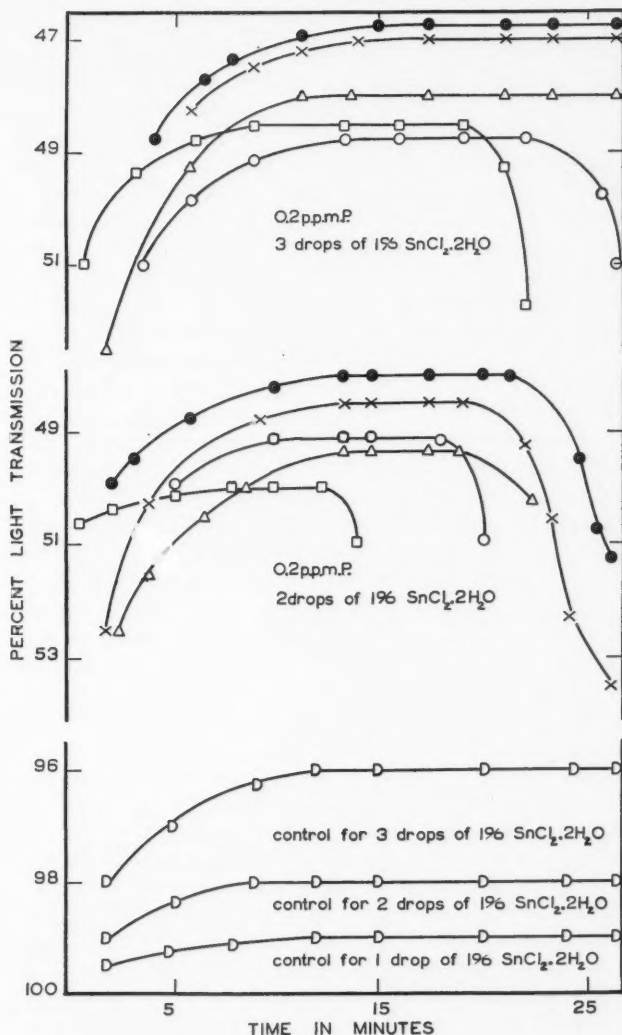

FIG. 8.   The influence of the ferric iron concentration on the behaviour of the colour, using two and three drops of 1% stannous chloride.   ● No ferric iron; × 5 p.p.m. ferric iron; △ 10 p.p.m. ferric iron; ○ 20 p.p.m. ferric iron; □ 35 p.p.m. ferric iron.   (Temperature of all solutions, 24° C.; 21 drops equal 1 cc.)

centration is higher, less iron is required to cause interference. For example, with a phosphorus concentration of 0.5 p.p.m., 10 p.p.m. of iron causes an abnormal maximum and rapid fading. In many instances it has been found possible to dilute extracts until the interference due to iron was no longer appreciable.

Since ferric iron will rapidly oxidize stannous tin to the stannic condition, it was thought that the iron interference might be due, in part at least, to this action. As has been shown, the concentrations of both stannous and stannic ions exert important influences on the colour development. Accordingly, the above experiment was repeated, two and three drops of stannous chloride reagent being added instead of the usual one drop. The results are given in Fig. 8. The iron interference is considerably decreased by using larger amounts of stannous chloride. Abnormal maxima do not occur even with 35 p.p.m. of iron, and the deviation from the normal curve is less at all the iron concentrations.

Various attempts were made to overcome the interference of ferric iron by adding reducing agents other than stannous chloride to the solutions. It was found, however, that these additional substances themselves had specific effects on the colour development, and hence served only to complicate further the interpretation of results. Also, the interference due to ferrous iron is technically a difficult one to avoid. The use of potassium cyanide, as recommended by Tischer (8), was found to be ineffective.

The interference due to ferric iron probably can be circumvented best by diluting the extract as much as the phosphorus content will permit (to 0.1 p.p.m. of phosphorus is a suitable dilution), and, if the iron interference is still appreciable, by using two or three drops of stannous chloride, instead of one drop. However, as already pointed out, the addition of larger quantities of stannous chloride will necessitate a correction for the colour development in the control solution.

Discussion

The nature of the so-called ceruleomolybdate reaction of phosphate ions is not thoroughly understood. The reduction of a variety of molybdate complexes to form blue-coloured products will proceed without the intervention of phosphate provided that the acidity of the medium is not too great. Berenblum and Chain (1) contend that the role of phosphate is that of a catalyst which promotes the reduction and is itself inactivated in the process, and there is good experimental evidence in support of this view.

The colorimetric behaviour is rather characteristic. The colour develops to a maximum, remains constant for a time, then fades quite rapidly, and finally very slowly. Substances which influence the reaction affect both the intensity and the stability of the blue colour, but the phases of development, stability, rapid fading, and subsequent stability are always apparent. No simple explanation of this typical sequence can be offered.

The behaviour of the colour is such that the reaction is not easily applied quantitatively. In the use of the photoelectric technique, precautions must

be taken to ensure that the calibration data are fully applicable to the solutions under test. The appreciable influence of temperature makes it necessary to establish the calibration constant that is currently valid each time readings are made. Calibration data obtained with pure phosphate solutions will not apply to solutions containing salts in appreciable concentrations. The appropriate calibration constant for such a solution must be obtained from the reading given by a standard phosphate solution containing the salts in identical concentrations.

The appropriate time for reading the colour maximum may not be generally prescribed, because of the probable differences between individually prepared stannous chloride reagents, and because colour stability decreases with increasing phosphate concentration. Each worker should determine the interval for taking readings that is appropriate under his own conditions. Gradual deterioration of the stannous chloride reagent may be avoided by storing it under an atmosphere of hydrogen.

The interference due to ferric iron is largely attributable to oxidation of the stannous ion. In all the practical instances so far encountered, the interference may be overcome by dilution and the use of excess stannous chloride reagent.

The ceruleomolybdate reaction of phosphates is extremely sensitive. The concentration of phosphorus in the final dilution should never exceed 0.5 p.p.m. and should preferably be about 0.25 p.p.m. Even minute amounts of perspiration and saliva contain enough phosphate to produce considerable errors. Consequently it is necessary to be unusually vigilant against contamination of the final solutions.

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s-DIPHENYLGUANIDINE AS AN ACIDMETRIC STANDARD[1]

By J. W. Young[2]

Abstract

s-Diphenylguanidine may be purified by recrystallization to provide a satis-
factory acidmetric standard. The results of titration of an alcoholic solution of
the base to pH 5.2 for N acid or 5.6 for $N/10$ acid agree within experimental error
with values obtained with sodium carbonate or borax. Three methods of
preparing borax containing exactly 10 molecules of water of crystallization have
been compared, viz., drying over sodium bromide, drying over a saturated solu-
tion of sugar and salt, and washing with alcohol and ether. Satisfactory products
resulted, but they were found to be unstable on storage. Sodium bicarbonate
has been found to be stable on long storage. The density of s-diphenylguanidine
at 20° C. was found to be 1.19.

The commonly used standards for alkaline solutions are in general satis-
factory, and may be said to meet the specifications proposed by various
writers (2; 7, p. 39; 10). The substances most generally used are potassium
acid phthalate and benzoic acid. The recent addition of furoic acid (6) has
provided at least three substances that are easily purified, are stable in air,
and contain no water of crystallization.

Unfortunately there are no completely satisfactory acidmetric standards,
and most commercial laboratories prefer to standardize acid solutions by the
use of a standard alkali that has been checked by one or more of the alkali-
metric standards mentioned. The two acidmetric standards most commonly
used are sodium carbonate and borax. Sodium carbonate is very hygroscopic,
must be freshly prepared from sodium bicarbonate or sodium oxalate, and may
be weighed only by the application of special precautions (8). Borax con-
taining exactly 10 molecules of water may be prepared by a time-consuming
process (8, 9), or by the use of special solvents (5). It is not stable with respect
to water content on storage or on exposure to air (5).

The use of s-diphenylguanidine was originally proposed by Carlton in a
preliminary study (1), but it has not been critically investigated. A recent
publication (11) records a preliminary study of this material and mentions
difficulty in the application of Carlton's method of purification.

Sodium bicarbonate has not been thoroughly investigated but appears to
have the merit of being stable in air (9).

Other standard substances, notably potassium iodate, calcite, and mercuric
oxide, have, owing to low equivalent weight, limited application, or difficulty
of purification, not received wide acceptance.

In this study the writer attempted to devise a suitable method for the
purification of s-diphenylguanidine, and to compare this standard with the
commonly accepted standards, sodium carbonate and borax. The various
methods of purification of borax were compared, and some observations were
made on the stability of sodium bicarbonate.

Apparatus

In all titrations a special burette was used.*   This instrument was built of Pyrex glass and consisted of a bulb of 49 ml. capacity attached to a graduated tube divided in 0.01 ml. from 49 to 55 ml.   A series of special temperature correction tables were prepared, and the instrument was standardized for various drainage times.   On the basis of these standardizations it was found that the probable error of determination of a delivered volume varied from 0.002 to 0.004 ml., the actual error depending on the amount delivered, the lower reading applying to volumes from 49 to 51 ml.

In use, the burette was adjusted to zero after the temperature of the contents had been read, and the acid solution was allowed to flow into the solution of base to be titrated with the cock full open until the volume of solution added was within 0.1 ml. of the end-point, as established by a preliminary titration. The titration was then carefully completed, and a series of volume readings taken at intervals of 5, 6, 7, 10, 15, and 20 min. from the start of the titration. Standardization curves using these drainage times were applied and temperature corrections made.   No differences could be detected between the drainage of normal hydrochloric acid solution and that of water, although the temperature corrections were of course very different.

In titrations of carbonate solutions the last 0.1 to 0.2 ml. of acid was added from a micro burette after successive boilings to remove carbon dioxide.

All titrations were made in Pyrex flasks, solvents being of the highest purity obtainable.   Blank titrations showed insignificant quantities of base in the alcohols used as solvents for s-diphenylguanidine.   Standardized weights were used, and all weighings were corrected to vacuum.

Preparation of Materials

Sodium Carbonate.   A sample of very pure sodium bicarbonate, free from chloride, sulphate, and potassium, was used as the source of sodium carbonate. This material was converted to sodium carbonate by heating in small crucibles to constant weight at 180° to 300° C.   These tests showed that sodium bicarbonate itself is very stable in air.   In using this supply, as stored in the stock bottle, the data in Table I were obtained.

Suitable quantities of sodium bicarbonate were weighed into crucibles, heated to constant weight, and the sodium carbonate was transferred to titra-

TABLE I

RESIDUES ON HEATING SODIUM BICARBONATE

Date	Aug. 12, 1935	Nov. 30, 1935	May 23, 1936	June 11, 1937
Residue at 280° to 300° C., %	63.143	63.148	63.144	63.147

* *This burette was built to the writer's specifications by the Scientific Glass Apparatus Company, Bloomfield, N.J.*

tion flasks with a stream of hot water.   The volume was made up to 50 ml.
and acid added to within 0.1 ml. of the expected end-point.   The solution was
boiled, cooled, and titrated to the end-point using the selected indicator and
a buffer mixture as standard.   The procedure of boiling and cooling was
repeated until no further acid was required.   Two such treatments were
usually sufficient.   The titration error using methyl orange and titrating to
pH 4.0 was found to be 0.014 ml. of N hydrochloric acid for a volume of
100 ml.   The titration error using brom cresol purple was not appreciable.

Borax.   Three samples of borax were prepared, all from a specially purified
grade.

Borax A.   This borax was twice recrystallized from water and dried for
eight months over sodium bromide.   It was stored in a stoppered bottle until
used.

Borax B.   This material was recrystallized in the same manner as Borax A,
but was stored for eight months over a solution saturated with respect to
both sucrose and salt.   It was stored as was preparation A (9).

Borax C.   This borax was recrystallized once from water, the wet crystals
were sucked as dry as possible on a Büchner funnel, and washed three times
with 92% ethyl alcohol and three times with ether.   It was dried for 30 min.
in air, and bottled (5).

The data in Table II were obtained on ignition of these preparations.

TABLE II

RESIDUES ON HEATING BORAX

Preparation	A	B	C	Theory
Residue on ignition, % September, 1937	52.765	52.790	52.796	52.769
October, 1937	52.819	52.844	52.819	

It will be noted that these preparations lost water over a period of one
month, during which they were opened for use in standardizations.   These
results confirm those of Hurley (5) and indicate the instability of borax on
ordinary storage.

Since the standardizations were performed at times between those of the
two series of determinations given in Table II, the mean values of these
residues on ignition were used in calculation of standardizations.

It was also noted that storage of borax in a warm place (40° C.) resulted in
loss of water of crystallization, which condensed in the upper part of the bottle.
Storage for one hour caused a loss of 0.64% in weight of 150 gm. of salt.

The procedure in standardization was to dissolve the weighed borax in
water (50 ml. in the case of 0.1 N acid and 100 ml. with N acid), add the

appropriate indicator, and titrate until a match was obtained with a solution prepared from sodium chloride and boric acid and diluted to the expected final volume of titration.

s-Diphenylguanidine.   The several methods used for purification had been tried on various batches of material in preliminary experiments, and had given satisfactory results in standardizations.   Quantities used were weighed to give final products weighing 100 to 200 gm.   Solvents were recovered by distillation and used several times.   Solutions were kept in Pyrex glass or porcelain, but were not protected from carbon dioxide in the air.   All products were dried at 90° to 100° C. and stored in stoppered bottles until used. Repeated analyses showed less than 0.02% moisture absorption on long storage.

s-Diphenylguanidine A.   Eastman Kodak Co. product.   Ash, 0.01%; m.p., 148.2° C.(d).

s-Diphenylguanidine B.   Material A, twice recrystallized from toluene. Yield, 81%; ash, 0.01%; m.p., 148.5° C.(d).

s-Diphenylguanidine C.   The base was dissolved in a minimum quantity of methanol, precipitated by dilution with water, filtered, and dried.   The dried material was recrystallized three times from toluene.   Yield, 73%; ash, 0.005%; m.p., 148.9° C.(d).

s-Diphenylguanidine D.   The residues from a series of titrations (the chloride salt of the base) were combined, precipitated with excess sodium hydroxide solution, and washed with hot water until free from chlorides. The base was dried and recrystallized three times from toluene.   Yield, 66%; ash, 0.015%; m.p., 148.9° C.(d).

s-Diphenylguanidine E.   The original material was washed with toluene, recrystallized once from toluene, dried, precipitated from methanol and water as with preparation C, dried, and recrystallized five times from toluene. Yield, 53%; ash, 0.01%; m.p., 149.0° C.(d).

In all cases, decomposition occurred above 100° C., as is noted in the melting point determinations.   Some decomposition may occur at lower temperatures, so a minimum time of drying was adopted in all cases.

The density of *s*-diphenylguanidine is not recorded in the literature, and a value was required for use in the reduction of weighings to *vacuo*.   Two determinations using heptane saturated with the base as displacing liquid gave values of 1.187 and 1.186 at 20° C.   Determinations in a gas volumeter of the type described by Francis and Oxnard (3) gave values of 1.16 and 1.18. The value accepted for this work was 1.19.

The method used in these titrations consisted in dissolving the weighed base in 40 ml. of the solvent selected using gentle heat, and titrating to the end-point with the acid.

The end-points used in this work differ from those adopted by previous investigators (1, 11).   Selected values were based on determinations of dissociation constants given by Hall and Sprinkle (4).   On the basis of their

results, in approximately 40% alcohol solutions, the end-points selected were pH = 5.2 for the titration of N acid and pH = 5.6 for $N/10$ acid.   In all cases the end-points were very sharp, being detectable to 0.005 ml. of 0.1 N acid.   A buffer mixture was prepared to contain the appropriate indicator at the proper pH.   In the case of methyl red the colours of alcoholic and aqueous solutions cannot be matched exactly, but the error was not significant.

Standardizations

The results of standardizations are presented in Table III.

TABLE III

ACID STANDARDIZATIONS

Standard substance	Solvent	Indicator*	Factors	Mean factor
N Hydrochloric acid				
Na$_2$CO$_3$	H$_2$O	M.O.	0.9959, 0.9957, 0.9953, 0.9951	0.9955
Na$_2$CO$_3$	H$_2$O	B.C.P.	0.9951, 0.9950, 0.9951, 0.9951	0.9951
Na$_2$B$_4$O$_7$A	H$_2$O	M.O.	0.9951, 0.9954, 0.9950, 0.9957, 0.9958	0.9954
Na$_2$B$_4$O$_7$B	H$_2$O	M.O.	0.9949, 0.9949, 0.9950, 0.9951	0.9950
Na$_2$B$_4$O$_7$C	H$_2$O	M.O.	0.9960, 0.9954, 0.9956, 0.9956, 0.9956	0.9956
C$_{13}$H$_{13}$N$_3$A	C$_2$H$_5$OH	M.R.	0.9959, 0.9962, 0.9962	0.9961
C$_{13}$H$_{13}$N$_3$B	C$_2$H$_5$OH	M.R.	0.9959, 0.9959, 0.9956	0.9958
C$_{13}$H$_{13}$N$_3$C	C$_2$H$_5$OH	M.R.	0.9953, 0.9954, 0.9955	0.9954
C$_{13}$H$_{13}$N$_3$D	C$_2$H$_5$OH	M.R.	0.9959, 0.9957, 0.9957	0.9958
C$_{13}$H$_{13}$N$_3$E	C$_2$H$_5$OH	M.R.	0.9956, 0.9957, 0.9955, 0.9957	0.9956
C$_{13}$H$_{13}$N$_3$E	CH$_3$OH	M.R.	0.9954, 0.9956	0.9955
C$_{13}$H$_{13}$N$_3$E	CH$_3$OH	B.C.G.	0.9957, 0.9957	0.9957
C$_{13}$H$_{13}$N$_3$E	*iso*-C$_3$H$_8$OH	M.R.	0.9958, 0.9959, 0.9957	0.9958
N/10 Hydrochloric acid				
Na$_2$CO$_3$	H$_2$O	M.O.	0.9819, 0.9817, 0.9819, 0.9824, 0.9823	0.9820
Na$_2$B$_4$O$_7$A	H$_2$O	M.R.	0.9819, 0.9824, 0.9819, 0.9826, 0.9824	0.9822
C$_{13}$H$_{13}$N$_3$B	C$_2$H$_5$OH	M.R.	0.9823, 0.9825, 0.9825, 0.9826	0.9825
C$_{13}$H$_{13}$N$_3$E	C$_2$H$_5$OH	M.R.	0.9824, 0.9820, 0.9826	0.9823

* Indicators—M.O., methyl orange; M.R., methyl red; B.C.P., brom cresol purple; B.C.G., brom cresol green.

In general, properly purified *s*-diphenylguanidine is a satisfactory acid-metric standard, giving results agreeing within 0.05% of those obtained with borax or sodium carbonate.   Methyl, ethyl, and isopropyl alcohols are satisfactory solvents for the base to be titrated, methyl red and brom cresol green being suitable indicators for the titration exponents selected.   The chloride salts obtained on titration may be used as a source of the free base which may be purified and used again.   The commercially available purified material gives results within 0.1% of those obtained with the purified base. The base is stable on long storage, attracting at most 0.02% of moisture.

Three methods of so preparing borax as to contain exactly 10 molecules of water of crystallization have been compared. All methods tend to give a product that is slightly low in water, and the material is not stable on ordinary storage.

It was noted that sodium bicarbonate shows stability on long storage, the composition remaining constant to 0.01% or better. The presence of carbon dioxide renders accurate titration difficult.

Acknowledgment

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